ON THE OCCURRENCE OF TIN IN ARTICLES OF FOOD AND
DRINK, AND ON THE PHYSIOLOGICAL ACTION OF TIN COMPOUNDS.

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IN July, 1878 (*Chemical News*, xxxviii., p. 971,) Mr. A. E. Menke first drew attention to the occurrence of tin in canned goods. He detected and determined the metal in pineapple, apples and in lobster. Mr. Menke's results have since been confirmed by other chemists; but as far as I am aware no extended series of analyses has yet been published, with a view to ascertain whether the presence of tin in canned food is exceptional or general.

In the case of acid substances, such as fruits, &c., one might fairly expect a notable solvent action upon the metal, but there appeared but little probability of any such action in the case of neutral or alkaline matters, such as meats, oils and milk. Mr. Wigner, in

his several papers in recent numbers of THE ANALYST, does not mention whether he found the samples, upon which he reported, to be free from tin, whilst Mr. Dyer, in a communication to one of the daily papers, expressly states that he did not detect tin in canned meats.

The *method of analysis* I adopted was as follows :—About 30 grammes of the article to be examined were incinerated in a platinum basin, the ash heated with strong hydrochloric acid, the acid for the most part boiled off; about 30 to 40 c.c. water added, boiled and filtered. This alternate treatment with acid and water was repeated, if necessary, until H_2S no longer indicated the presence of tin. The clear and, as a rule, colourless solutions thus obtained were precipitated with H_2S , and the precipitate thus obtained, when necessary, further treated in the usual manner.

The following *vegetable foods* all gave abundant yellow precipitates of stannic sulphide :—

French asparagus, American asparagus, peas, tomatoes, peaches (three different brands), pineapple (two different kinds), white cherries, red cherries, marmalade.

In several cases the inner surface of the canister was found much corroded. So considerable is the proportion of dissolved tin in most of the acid fruits, that tin reactions can readily be obtained from two or three grammes of the substances. A metallic taste is sometimes perceptible.

The following *animal foods* were examined :—

Corned beef (five different brands), ox cheek, ox tongue (three kinds), collared head, tripe, oysters, sardines in oil, salmon, salmon cutlets, lobster, shrimps, curried fowl (two kinds), boiled rabbit, boiled mutton, roast chicken, roast turkey, ox cheek soup, gravy soup, sausages, condensed milk (three brands).

With the exception of the sausages the whole of these samples contained more or less tin. The amount found in one of the soups was 35 milligrammes of tin in one pound canister; in a tin of condensed milk 8 milligrammes; in a pound tin of preserved oysters 45 milligrammes, besides a considerable quantity of copper.

The metal is to be found throughout the mass of the liquid soups and pasty curries, but resides chiefly on the outer surface of hard meats, such as corned beef. In many cases the canisters were much discoloured and blackened on the inner surface, but in others the surface of the metal was perfectly bright, although there was an abundance of tin in solution.

From the results given, it appears, beyond doubt, that tin is most readily acted upon by articles of food, vegetable and animal. Vegetable acids dissolve it abundantly, even if the contact be only of very short duration. Several samples of *ginger ale* and *lemonade*, which I have recently tested, gave distinct tin reactions. Even carbonic acid attacks the metal. In aerated waters kept in syphons, the mountings of which consist of pure block tin, the metal is almost invariably found in solution, and on shaking pure tin filings, or tin foil, with carbonated water, a sufficient amount of tin dissolves in a few days to produce a marked colouration with H_2S . The metal dissolves as a stannous compound, and H_2S gives a brown colouration. Now, seeing how frequently aerated beverages are reported to be impregnated with lead, and yet how rarely lead enters into the composition of the pipes and cylinders of soda-water machines as now used; considering further the difficulty of identifying lead when present only in traces, I cannot but believe that in many cases tin has

been mistaken for lead. Metallic tin readily precipitates lead from its solutions, and even from tin containing lead acids do not extract the lead until much of the tin has dissolved, and the proportion of lead in the residue has become considerable. Thus from solder lead can be dissolved simultaneously with the tin. I would advise, therefore, in testing aerated beverages for metallic contamination, to oxydise any stannous salt present, by the addition of a few drops of chlorine water, and after the expulsion of the excess of chlorine to test with H_2S . If a *black* colouration be then obtained, and copper be absent, the presence of lead can safely be declared.

It also follows, that there is but little danger to be apprehended from the employment of impure tin for the manufacture of tin plates. The tin effectually protects the lead from being dissolved. It is from the solder that contamination with lead might ensue.

Seeing then the general occurrence of tin in canned foods, and in articles of drink, the question naturally suggests itself,—*Is tin, when taken into the system, injurious to health or not?*

The opinions of toxicologists on this point seem to be somewhat divided, and not very pronounced. Most of the works on the subject do not refer to it at all, whilst Taylor dismisses the compounds of tin in his work on "Poisons" with half a dozen lines. According to Woodman & Tidy (*Forensic Medicine*, p. 229), the chlorides of tin are accredited with being active and irritant poisons. Orfila states that oxide of tin is likewise poisonous, but this assertion has been contradicted by others. Pereira, again, declares that chloride of tin acts topically as an astringent, irritant and caustic, and that when taken as a poison, it causes convulsive movements of the muscles of the extremities and of the face. Some poisoning cases, of old date, are likewise on record, one with fatal result.

No doubt the condition of the compounds of tin would, to a great extent, determine whether or not they would prove injurious. Thus tin chloride might be expected to show physiological action, whilst ignited stannic oxyde from its insolubility would prove harmless. The state of oxydation might also modify any action; thus one would conjecture that stannous compounds would be more active than stannic salts. Under the circumstances obtaining in canisters in which food is preserved, stannous compounds in a hydrated and soluble form would predominate.

The following experiments may prove interesting, especially since the physiological action of the compounds of tin is but very partially studied:—

A half-grown, apparently healthy guinea-pig took with its ordinary food 25 milligrammes of tin in the form of *stannous hydrate*. This had been freshly precipitated, and had not been dried, but was given shaken up in water. There was no apparent effect. The solid excreta contained much tin after the lapse of a few hours, whilst the metal could not be detected in the urine. Two days afterwards the animal took 50 milligrammes of tin, as stannous hydrate. After three hours it appeared ill. Next morning it was dead. The quantity of *fæces* passed since the administration of the second dose was very small, and the size of the *fæces* had diminished extremely, about to that of those of a mouse. On dissection the stomach was found practically empty, the colon distended with food, the small intestines empty. The liver, kidneys, lungs and heart were separately examined. They all contained traces of tin, the largest quantity being apparently in the

liver. The main part of the dose given, however, remained in the food contained in the colon, so that comparatively little of the oxyde had been dissolved and absorbed. Death therefore had been produced by a far smaller quantity than that administered, and was apparently due to the astringent and irritant action of the metal.

Another somewhat stronger guinea-pig took 30 milligrammes of tin in the form of *stannic hydrate*, also freshly precipitated and moist. As no ill effect seemed produced, another 45 milligrammes was given on the same day. The fæces contained much tin. Next day the animal further took two doses of *stannic hydrate* of 75 milligrammes in each. A few hours afterwards it appeared ill; its abdomen was distended, whilst the fæces were diminishing in size. Next day the pig seemed quite well again, and took, without apparent ill effect, three doses of 75 milligrammes each. Thus altogether it had in three days 450 milligrammes of tin, as *stannic hydrate*, without much injury, although the astringent effect of the tin had become visible.

On the day following, when it seemed in perfect health, it took 50 milligrammes of tin in the form of *stannous hydrate*. It was ill next day, and did not take any food until its death, three days afterwards. The few excrements passed during that time were very small, much like those observed in the case of pig No. 1. They contained much tin. The stomach was practically empty; the colon and bowels filled with semi-fluid green offensive matter, containing much tin. The liver contained a notable quantity of tin, and the lungs, heart, and kidneys, traces of the metal.

From these experiments, it appears that whilst *stannic hydrate*, from its comparative insolubility in gastric juice, is without much effect in the doses given, *stannous hydrate*, very soluble as it is in dilute acids, is a powerful irritant poison.

The spasmodic twitching mentioned by Pereira was quite pronounced in the case of animal 2.

It would be interesting to ascertain whether tin, when given continuously in small doses, accumulates like lead.

Canned goods are doubtless but rarely consumed so continuously and in such quantity as to be positively poisonous on account of the tin they contain dissolved, although circumstances are imaginable, as on board ship or on Arctic expeditions, under which poisonous symptoms might become pronounced. But even the occasional consumption of such goods, containing as they do a poisonous metal in a soluble form, *cannot but be more or less injurious*. Of the mysterious poisoning cases recently repeatedly traced to canned goods, the tin may possibly have been the cause. Knowing, then, that such articles of food do constantly contain more or less tin, the employment of tin canisters, of tin saucepans, and tin cooking utensils, ought to be much discouraged by Public Analysts and by medical men. The danger may be small, but every item which is inimical to the health of human beings ought to be avoided when once pointed out. On the same principle, we condemn the presence of copper and lead, even in small quantities, in articles of food and drink.

The trade in canned goods is one of enormous magnitude, and the subject of the purity of these goods is one proportionally important. Surely, human ingenuity will devise means to protect the substance of the canisters from being attacked and corroded by the contents. Such protection has already been attempted more than once, many of the French preserved vegetables being put up in canisters varnished on the inner surface. The varnish is,

however, burnt away on the seams during the closing of the tins, leaving the solder exposed, and thus not only tin, but lead, is frequently found in the contents of such "protected" goods.

Dr. Wynter Blyth said it struck him as possible that Mr. Hehner had rather too readily assumed that the tin in the meat and the vegetables he had examined was in a soluble form, but it was he (Dr. Blyth) thought more likely that very minute particles of tin had been rubbed off by the mere friction of the vegetable or meat, and therefore if it was of frequent occurrence in tinned meats, they had to deal with the question of whether tin in a metallic state was poisonous. When he was in medical practice he frequently gave metallic tin in a finely divided state, and he had certainly never seen any bad action follow. He had given at least 350 milligrammes in a finely divided state, and seen no deleterious action arise from it. With regard to the black precipitant it was well not to be too hasty in putting down that as lead. He had always found considerable difficulty in discriminating between dark discolouration when there was only that to work upon, and that was all there was when there was a mere trace in water. With regard to the symptoms about the excrement being small, it struck him as being on account of the loss of appetite.

Dr. Dupré said that in lemonade the lead was traceable to the citric acid used, where, although the action of the lemonade on the vessel in which it was contained was slight, it was nevertheless almost impossible to get citric acid or tartaric acid free from lead.

Mr. Dyer said that the letter, to which Mr. Hehner had referred, was written just after an inquest on a child, who had died from eating poisonous tinned meat (or supposed so). Everyone who had tasted it had experienced symptoms of poisoning. The medical man who attended the child did not appear to have made any analysis either of the meat or of the stomach, but he expressed an opinion that the death was due to metallic poisoning, and suggested that it was owing to the hydrochloric acid used in the process of soldering having dissolved some of the tin. He had also had another case, of ox tongue. Cases of poisoning were by no means confined to *tinned* meats, many cases happened with untinned—for instance, with sausages. Referring to another point, he wished to ask if any member had had any experience in finding the presence of small quantities of zinc. He had had cases of water being contaminated with small quantities of zinc, evidently derived from galvanic tanks. He wanted to know what quantity was considered dangerous. The point seemed rather obscure.

Mr. Wigner said, having had much experience in all kinds of canned goods, he was sure that 20 or 30 milligrammes of tin in the pound could be detected by the taste. He had as yet only found one sample of canned fish which was free from tin present in the fish. This was a tin of prawns, and they had probably been canned less than a month. He did not think that in the case of fish it was merely as Dr. Blyth had suggested, the mechanical adherence of the tin. In nearly every case condensed milks, which had been kept more than a month or six weeks, tin and lead were both present. As to the meats, he had during the late Food Exhibition examined something like 50 different brands of Tongues, Hams, Chicken, Corned Beef, Roast Beef, &c., and there was only one tin (or brand) in which tin was present in any appreciable quantity; equal to about 0.5 milligrammes in the pound instead of the 10 milligrammes spoken of by Mr. Hehner. He believed the solder, used to

fill up the blow holes of the tins, most frequently contained bismuth, and that was at the bottom of the galvanic action which was set up. In the last number of THE ANALYST he referred to a very old can of meat, which was free from tin. With regard to canned fruits he had tried more than 300 varieties, and only about 8 or 10 had turned out bad. He thought an alteration in the character of the tin, or rather of the tinning, would meet the difficulty.

Mr. Hehner, in replying, said he did not think there was the slightest doubt that the tin was in a dissolved state, for it was found not only in solid meats but in soups and curries and in compressed meats; also one could plainly see that it was not metallic tin; it was not only on the outer surface that the tin was found, but in the parts near the surface as well. He thought Mr. Wigner was very fortunate in getting samples free from tin, as he himself had obtained his indiscriminately, and invariably found tin.