A FURTHER NOTE ON LEAD IN CANADIAN CHEESE.

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ON page 208 of the current volume of the ANALYST is a report of a short communication I made to the Society on cheese containing lead in what I believed to be largely the metallic condition. The evidence on this point, however, was not of the most conclusive character, as was pointed out by several contributors to the discussion that followed.

The physical characters of the material seemed to limit the possibilities to the metal more or less superficially corroded, the sulphide, and to certain salts such as the carbonate blackened by sulphide resulting from decomposition of the cheese. The difficulty in deciding arose, of course, not so much from the want of analytical methods, as from the impossibility of freeing the matter from adherent particles of cheese. It should be remembered that the total lead amounted only to $1\frac{1}{4}$ grains per pound of cheese, that most of this was so distributed over the surface of the curds as to be inseparable by scraping, and that any attempt at destruction of the adherent matter defeated the object of the experiment by attacking the pigment.

My reasons for arriving at the conclusion stated were the solubility relations to acids, particularly to dilute nitric acid in the cold, the purity of the oxide obtained on ignition, and the entire failure to detect sulphur in any shape; to these may be added the readiness with which the substance was attacked by caustic alkali in attempts to purify it.

As regards the detection of sulphide, it was suggested by Mr. Allen that a good method consisted in treating with hydrochloric acid in presence of zinc, when sulphuretted hydrogen is readily liberated. This reaction has been applied without demonstrating the presence of sulphide. It seemed, therefore, very desirable to obtain positive evidence as to the condition of the lead, and further consideration has suggested a method which apparently yields decisive results.

It is well known that lead ranks amongst the more electro-positive metals, and that many others, especially silver and copper, are readily deposited upon it from slightly acid solutions. A stick of lead immersed in a slightly acid solution of copper is speedily covered with a closely adherent film of characteristic colour. If this film is scraped off with as little lead as possible, and the metals precipitated from solution in acetic acid with a ferrocyanide, the lead ferrocyanide formed is tinged more or less deeply with the red copper ferrocyanide. This forms an exceedingly delicate test for copper, the least shade of red being very perceptible. Under parallel circumstances, silver is deposited as a brownish black pulverulent coating rather easily detached by rubbing.

It appeared to me that these reactions would be applicable to the problem in hand. By working over ten or twelve pounds of cheese, and selecting the best bits, about half a gramme of material rich in the black pigment was obtained. This was rubbed down in alcohol, and, after decantation of the latter, thoroughly exhausted with ether; it was then washed successively with alcohol and water. After decanting

as closely as possible, the moist residue, consisting now of the pigment with perhaps five times its bulk of casein, was divided into two parts, and treated with silver nitrate and copper sulphate respectively. In a few minutes a distinct change of colour was observable in the silver experiment, the mass taking a brownish shade. Both tubes were left for thirty minutes, then washed with hot water until the washings gave no reactions for metals; the residues were then treated with warm dilute nitric acid, when the filtrates gave abundant reactions for silver and copper respectively. The precipitate of silver chloride so obtained weighed 9 milligrammes, representing about 6 milligrammes of metallic lead. The reaction appeared less complete in the case of the copper.

Now, a possible objection—the only one, as far as I can see—to this experiment is based upon the known affinity of proteids for the heavy metals, notably for copper; and it may be suggested that the casein remaining adherent to the pigment may so far fix either copper or silver as not to yield it to water, though it may subsequently do so to nitric acid. Blank experiments, therefore, were carried out side by side with that described above, using a considerably greater quantity of (a) sound portions of the cheese under examination, and (b) cheese from an entirely different source. Of these blank experiments, those with silver yielded in the final stage a distinct opalescence of chloride, showing that a trace of silver was rendered insoluble in water. No reaction was obtained with the copper under the same conditions, but a more rigid examination showed that a minute quantity of copper was fixed. The amount, however, in both cases was so minute in comparison with that obtained in presence of the black pigment, as to be negligible for the special purpose in view.

I think, therefore, I am justified in concluding that the black pigment consists essentially of metallic lead, with possibly some superficial sulphide.

As to the origin of this impurity, no light has up to the present been obtained. The most reasonable suggestion seems to be that it is introduced accidentally by friction upon some leaden surface. This explanation would be consistent with the fact that out of a consignment of two hundred cheeses about one hundred and fifty were affected in varying degrees.

An interesting point is that for many months mice refused to eat this cheese, though they repeatedly disposed of the greasy paper in which it was wrapped; and only very occasionally, and to a very limited extent, was the cheese itself attacked. On the other hand, during the last few weeks it has become such a happy hunting-ground for “jumpers,” the larvæ of a small black fly, as to necessitate its destruction.

DISCUSSION.

Mr. ALLEN said it was no doubt a very curious thing that the lead should be present, and one began to speculate as to its origin. He had heard of cheese being wrapped in cloths impregnated with chromate of lead, and it occurred to him to ask if Mr. Stoddart had looked for chromium in any form. It was possible, in the case of the heavy metals, that they might be reduced from such a compound as a chromate to a metallic state by reaction with the organic constituents of the cheese. Personally he was not satisfied as to the condition in which the lead existed, but Mr. Stoddart had taken a great deal of trouble in the matter, and it was not easy to decide as to

the condition of a substance existing in such a finely-divided state and such small quantity in an article like cheese. Whatever its origin might be, however, there could be no doubt as to its existence, and it behoved public analysts to do all they could, in cases like this, to ascertain, if possible, how the impurity came to be present.