

ON THE RECENT DISCOVERY OF
COPPER IN ORGANIC MATTERS,
CONSIDERED WITH RESPECT TO CASES OF
POISONING, OR THE ADULTERATIONS OF
FOOD.

(Read before the Westminster Medical
Society, Saturday, March 5.)

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THE manifest importance of the subject to which I have taken the liberty of requesting the attention of this Society, will I trust relieve me from the imputation of consuming their valuable time in idle and profitless speculations. An inquiry into the medico-legal value of chemical evidence in deciding on the presence of any deleterious substance in a suspected compound, no matter what the poison may be, must, if properly conducted, be attended with a certain degree of advantage to the public remotely, and more immediately to the medical profession. The interest of the inquiry is of course proportionate to the virulence of the destructive agent, and in this respect the preparations of copper undoubtedly occupy a very prominent place.

In the brief remarks which I proceed to offer, I mean entirely to restrict myself to the value of *chemical* evidence in deciding on cupreous poisoning or adulteration. With the semeiology or pathology of these cases, I shall not interfere, partly because these subjects have already been investigated with an ability and precision which scarcely admit of any improvement, but principally that I should not distract attention from a point in itself of sufficient importance. Moreover, for many reasons, chemical evidence of poisoning constitutes a distinct and insulated subject; for example, it not unfrequently happens, that from the unfortunate lack of analytic habits in the general body of practitioners, a suspected substance is sent from a distance for analysis, in which case the examiner is usually unaided by the history of the case in arriving at his conclusions. Again, in cases which do not prove fatal, as in feigned or imputed poisoning, or in accidents from spoiled food, or in casual concurrent vomitings or sporadic cholera in individuals, the chemical analysis is almost of exclusive importance. Lastly,

adulterations of food we have scarcely any other guide to conduct us to a correct decision, inasmuch as it but rarely happens that adulterators are so incautious or unskilful as to add such quantities of any poisonous ingredient, as might indicate the use by its speedy physiological effects.

Having premised these general remarks, I proceed to state that the object of the preceding observations, is, to prove that the natural existence of the oxide of copper in various organic substances, first, that the detection of minute quantities of that metal in suspected cases affords, *per se*, no grounds of imputation; secondly, that in all cases of analysis it is absolutely necessary that the quantity of the copper detected should be accurately estimated. As far as my limited information extends, no attention has yet been paid to these circumstances by medico-legal authorities. At least, the latest and best work of this description is totally silent on the subject.

The existence of the oxide of copper in organic matters was first noticed and demonstrated by the celebrated Assessor Gahn, of Fahlun, who was accustomed to exhibit the production of distinct particles of metallic copper reduced by him with the mouth-blowpipe from a quarter of a sheet of burnt paper. Singular as was this fact, it seems to have for some time attracted but little attention. The next experiment worthy of record on the subject, is stated by *Bucholz*, who detected copper in the ashes of the *anonium zedoaria*, in the galanga root, in others of the same family, and in various other vegetables of distinct kinds. These researches were pursued by *Meisner* with further success; and, lastly, *M. Sarzeau* has shown in the *Annales de Chimie* for July, 1830, that not only does copper exist in the plants enumerated by Meisner, but in various products of the animal department of organization. I should also say that in the admirable and highly-useful translation of *Rose's Manual of Analysis*, just published in this country, it is stated, that copper may be detected in solutions of sugar by a reagent to which I shall presently have occasion to revert.

Of these experiments, those of *M. Sarzeau* are, in a medico-legal point of view, by far the most important. He enumerates cinchona bark, two kinds of coffee, cheese, and blood, as substances in which he has detected minute quantities of the metal; and in coffee, he states it to exist to the extent of a grain in the pound. The process by which *M. Sarzeau* proceeded, was by drying and incinerating the substances for examination, treating the ashes with dilute nitric acid, saturating the solution with ammonia, which throws down several foreign matters, still retaining the

copper in solution. The mixture is then slightly acidulated with acetic acid, and the few drops of ferrocyanate of potash added. The first effect occasioned is the production of a brownish tinge, which deepens in some hours, and in the course of twenty-four hours (in some cases longer), a brown flocculent precipitate is deposited, the ferrocyanate of the oxide of copper.

To obtain the metal from this precipitate is exceedingly easy. It consists in heating the precipitate to redness on a porcelain capsule, by which the hydrocyanic acid is partly expelled, and partly retained in combination with the oxide of iron, leaving on the capsule a mixture of the peroxide of copper, and the blue hydrocyanate of iron; on this you act with a little dilute sulphuric acid, which dissolves both metals, and by the addition of ammonia the iron is precipitated, and the copper retained in solution as before. You have now but to filter, acidulate with a little sulphuric acid, and introduce a bit of pure iron wire, which shortly becomes coated with metallic copper.

Since the publication of *M. Sarzeau's* paper, I have repeated the process with every precaution against fallacy I could devise, being impressed with the idea, that if I obtained similar results, they should induce medical jurists in this country to be cautious in deciding on poisoning or adulteration by copper on chemical evidence.

I first procured a sufficient quantity of nitric acid and ammonia to serve for all my experiments, and lest the copper might be contained in either of these fluids, I neutralized a portion of one with the other, dropped in the solution of ferrocyanate of potash, and patiently allowed them to stand for ten days, and not the slightest effect was produced; no fallacy was therefore to be apprehended from the materials employed, and this, I may remark, is by no means an unnecessary precaution, for I have more than once known a reagent to test itself, if I may be allowed to use the expression.

1st. The first experiment was with 10 $\frac{3}{4}$ of unroasted Berbice coffee; in 24 hours a dense precipitate occurred, which, by the necessary manipulations, coated two inches of harpsichord wire with metallic copper.

2nd. Fourteen ounces of white bread were similarly treated; a cupreous precipitate showed itself in minute traces in 24 hours, and in three days was sufficiently considerable to admit of decantation, incineration, and reduction by the immersion of the iron wire.

3rd. Eight ounces of black mustard-seed gave a similar result.

4th. One pound of beef afforded a faint metallic crust.

5th. From 16 $\frac{3}{4}$ of human blood, distinct

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rares of copper were obtained at the end of six days.

6th. Three pounds of potatoes gave no cupreous marks; 1 lb. of pine charcoal seemed equally devoid of metallic impregnation.

7th. The last experiment I instituted, was one to which I would especially request the attention of the Society. I prepared an alimentary mass, such as I conceived might exemplify the rejected matters after a meal, perhaps, attended with suspicious circumstances. The mass consisted of two eggs, three cups of strong coffee, and eight ounces of bread and butter. On drying and incinerating this mass, and subjecting it to the other steps of the process, metallic copper was distinctly obtained.

Concerning the source of the copper thus detected, I shall not at present enter into any speculations, further than to remark, that with respect to bread, some difference of opinion may arise whether the copper actually exists in the corn, or is accidentally or designedly introduced during the subsequent steps of the preparation of bread. In support of the natural existence of the copper in corn, we have, first, the analogy of its undeniable existence in other vegetables; secondly, the evidence of M. Lefebure, a Dutch chemist of high reputation, who declares that he has found it in corn; and, thirdly, I may add my own experiments on bread, in which no adulteration of this kind has, in this country, been suspected. In opposition to these opinions, and in support of the designed adulteration, I may adduce the recent conviction and confessions of several bakers in Belgium, for practising this adulteration; secondly, in my own experiments, I have never succeeded in tracing copper in corn itself, although I have operated on a specimen growing over an extensive stratum of copper ore. That the copper may occur in bread accidentally, I conceive may arise from the *debris* of mill-stones, which, in some districts, are, I am told, incorporated with malachite or the carbonate of copper; and, lastly, from the evidence of M. Ludibert, who, in a debate on this subject at the *Académie Royale de Médecine, séance de Janvier, 1830*, stated that the sulphate of copper was used for the prevention of the mauling of grain. My own impressions on the subject are, that copper usually finds its way into bread by accident. The Belgic bakers used it by mistake for blue alumin. However, my experiments as yet have been too limited to enable me to pronounce a positive opinion on the subject.

However this question be decided, it is manifest that the natural existence of copper in the other substances I have described, must exercise an important influ-

ence over medico-legal analysis. One observation I will advance on this subject. The Society, perhaps, are aware that a work of the odd appellation of "Disease and the Pot and the Bottle" was published in London last year. Amidst other observations, it announced that the green Stilton cheese was sometimes cured by the use of verdigris; I accordingly procured a quantity of the green cheese, and substituted on it nearly the same experiments recommended by M. Sarzean, and detected metallic copper. I can only say, that the appearance of M. Sarzean's paper provoked my denouncing the supposed adulteration to the local authorities, and on repeating the process with cheese not greened, I obtained an equal quantity of copper was obtained.

I have now, I trust, advanced enough to bear me out in my assertions; 1st, the chemical grounds alone the detection of minute quantities of copper affords no grounds of imputation; and, 2nd, that in all cases of analysis it is absolutely necessary that the quantity of the detected copper should be accurately estimated. I proceed, in conclusion, to detail a process by which the last object may be accomplished.

The points to be attended to in the quantitative detection of copper are four: 1st. To bring all the copper in the suspected mixture into a state of solution. 2dly. To free that solution from organic matter as much as possible. 3dly. To throw down from the solution an insoluble compound of copper, the combining proportions of which are well known; and lastly, to reduce that insoluble compound to the metallic state.

The first of these objects, namely, the dissolving of the copper, is readily and certainly effected by boiling the suspected material in dilute nitric acid for an hour in a porcelain vessel glazed with porcelain. The best vessels of this description, I may remark, are imported from Hamburgh, and others should be used when these can be obtained.

The second point, viz., the freeing the solution from organic matter, is best obtained after the necessary mechanical filtration by the addition of caustic ammonia, which throws down caseum, albumen, the oxide of iron (which is often present), and various earthy matters, such as the phosphate of lime, while it retains the oxide of copper in solution.

The third step consists in the transmission of sulphuretted hydrogen through the mixture previously acidulated with acetic acid. An insoluble sulphuret of copper is formed, which readily subsides after boiling, and may be collected on a small filter. However, as the sulphuret of copper thus

obtained is always associated with organic matters, it should be incinerated on a little porcelain capsule over the spirit-lamp flame, and the residue redissolved in dilute sulphuric acid. This fluid is again to be neutralised with ammonia, a little acetic acid added, and sulphuretted hydrogen again transmitted. The sulphuret is now quite pure. It should then be washed, removed, dried in a water-bath, and carefully weighed. Of this black sulphuret—

100 Parts correspond to 64 metal	
Gr. 80 peroxide	
1 Grain	2 anhyd. sulph. of copper
.....	3 $\frac{1}{2}$ crystallised ditto
.....	1 $\frac{1}{2}$ neut. anhyd. per acet.
.....	2 $\frac{1}{2}$ crystallized ditto
.....	1 $\frac{1}{2}$ anhyd. carbon. copper
.....	1 $\frac{1}{2}$ crystallized.

Lastly, this sulphuret should be reduced to the metallic state by boiling it with a little dilute nitric acid in a test tube, neutralising with ammonia, which strikes a beautiful blue colour, reacidulating with sulphuric acid, and introducing pure iron wire.

The reasons why I prefer this process to that of incineration and precipitation by the ferrocyanate of potash, are briefly, because the sulphuretted hydrogen does not indicate copper in the substances in which that metal naturally exist; and secondly, because the combining proportions of the ferrocyanate of potash have not yet been ascertained with sufficient precision.

Before I conclude, there is one point which I would remind the Society is of vital importance to be attended to in our inquiries on any fatal case of poisoning by this metal; it is, whether a cupreous emetic has not been administered before death, and if it has been, what was the precise quantity of the dose? It is obvious, that a professional poisoner might endeavour to protect himself from suspicion and conviction by the open administration of a copper emetic, under the pretence of ridding the stomach of any deleterious and unknown substance. In such a case it is evident, that if to our question as to the quantity of copper contained in the emetic, he replies, five grains, and that on analysis we find sulphuret of copper equivalent to twelve grains, that the chemical evidence is as conclusive as if seven grains had been detected where no emetic had been given.

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