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PRELIMINARY NOTES ON THE COLORIMETRIC ESTIMATION OF MINUTE QUANTITIES OF LEAD, COPPER, TIN, AND IRON.

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(Read at the Meeting, April 4, 1894.)

WE frequently have occasion to examine samples of liquids containing traces of metals derived from impurities in the ingredients employed in their manufacture, or now more frequently arising from solution of metallic surfaces of machinery with which the liquids come in contact in process of preparation. We may say that in the latter case we find strong evidence in support of our view that the nature and causes of such metallic contamination have hitherto not received sufficient consideration at the hands of many well-known analysts, and have, indeed, in our opinion been in several important cases (of course, quite unintentionally) mis-stated.

There can be very little doubt that some modified gravimetric process would be preferable in many cases of examination of samples of mineral waters and allied aerated beverages. A process of this nature was suggested and carried out with admirable results some time since in cases in which we had the privilege to be associated with Mr. Otto Hehner. But it frequently happens that the analyst is compelled by smallness of sample, or other equally potent reasons, to adopt some process involving a smaller expenditure of material and time. We may, perhaps, be allowed to say incidentally that in our opinion the *time* occupied in commercial analysis does not always receive its due recognition, and it seems very desirable that there should be more uniformity in fees for different classes of work. But, be that as it may, as a matter of fact it is often necessary to employ some form of volumetric process.

The method most frequently adopted appears to be that originally suggested by Miller, in which the solution (rendered acid, or alkaline, according to the class of metal required to be estimated) has a certain quantity of sulphuretted hydrogen in aqueous solution added, and is then compared with a solution containing a known quantity of the same metal similarly treated. The process is, of course, closely comparable with the Nessler test, familiar to every water-analyst, and it gives fairly good results if only one metal be present. In many laboratories a very small quantity of ammonium sulphide solution is used in place of the sulphuretted hydrogen solution, the test being made in the manner suggested by Wanklyn.

Although we find that this method possesses some advantages (in the case of water-analysis, for example), we have, nevertheless, found many practical disadvantages attending its use in some other classes of work, notably in the case of

liquids possessing a slight yellow tinge in the first instance. And, further, we find no little difficulty in attaining uniform tint in the porcelain dishes in which this test is usually conducted.

We have, therefore, adopted a form of Nessler glass for tests of this description, and invariably use freshly-prepared sulphuretted hydrogen solution. We also find it almost essential for obtaining really accurate results to adopt some form of screen which allows white light to pass vertically only through the Nessler cylinder. We had some difficulty at first in obtaining glasses of uniform colour. But by selecting (by kind permission of a firm of manufacturers) glasses from a large stock, we obtained some few sufficiently good for ordinary purposes.

As we found that some curiously contradictory results were occasionally obtained, we were led to note carefully the conditions under which uniformity was possible. Of course, such results would only be noticed by those whose position brought into the laboratory a very large number of samples of one class of goods.

As the result of these observations, we thought it desirable to make a large number of experiments under varying conditions, and we have the honour to lay before the society a very brief epitome of some of the results obtained, in the hope that new suggestions may be made, and better methods of work suggested. For papers are only of value when they induce fresh investigation and improve our common work. If it be wished, we can give some of our work in greater detail, but it seems to us undesirable to over-burden the journal with excessive detail, or to make papers for the purpose of attracting attention to individual workers.

For purposes of comparison, we prepared standard solutions of such strength that 1 cubic centimetre contained 0.0001 gramme of metal. The method of making the test was as follows :

An empirical solution of any given metal was made, and a certain amount added to filtered distilled water in a Nessler tube, and made up to exactly 50 c.c. with similar water ; then a few drops of acetic acid were added, and finally about 2.5 c.c. of a fresh saturated solution of sulphuretted hydrogen in water.

The same process was carried out with the substitution of the standard metal solution (in the proportion requisite for giving a precisely similar tint) for the empirical metallic solution, and the strength of the latter thus determined.

But in the case of the standard solution, the sulphuretted hydrogen solution was sometimes added to the water before the addition of the metallic solution, and at other times the metallic solution was added before the introduction of the sulphuretted hydrogen. It was found that a very important difference arose in the two different orders of addition. For instance, in the experiments with an unknown quantity of lead acidulated with acetic acid, to which sulphuretted hydrogen was *subsequently* added, it was found that when the attempt was made to produce the same tint by adding the standard lead solution to the water *already* mixed with the requisite amount of sulphuretted hydrogen the difference amounted to 0.1 c.c. and upwards in the quantity required. Though it was found that in the case of very dilute lead solutions fairly uniform results could be obtained.

Experiments of a similar character with copper gave also very discordant results. For instance, in three successive tests 3.5 c.c., 4.0 c.c., and 4.2 c.c. were

respectively used to secure similarity of tint, giving a difference of 0.7 c.c. between extremes, arising from difference of order of addition of reagents.

We next passed on to experiments with mixtures of metals, since it often happens that several metals are present in fluids with which we are practically concerned. We may mention at this point the value which we found in Dr. Teed's suggestion (made in a paper read before the society some time since), that the coloration, due to the presence of copper, might be prevented by addition of potassium cyanide, while, when iron also is present, its influence on colour reactions may be avoided by the employment of tartaric acid. It is, perhaps, hardly needful to say that this latter must be absolutely pure, and that the tests must be made in alkaline solution.

Certain difficulties, however, arise when other metals are present, to which we shall have occasion to refer subsequently, although Dr. Teed's method possesses great value in many cases.

For experiments on mixed metals we employed solutions containing varying proportions of standard metallic solutions, as we had reason to believe that difficulty would arise in the direction of tints of matching solutions. For it should be noted that in the case, for instance, of lead and copper the tint given in each case by the addition of sulphuretted hydrogen differs widely. In fact, it is practically impossible to carry out the volumetric process with mixtures of some metals on account of the complexity of tints.

We first experimented with copper and lead in the following way: Taking a mixture of equal quantities of solutions containing approximately the same amount of lead and copper, we found it impossible to match the colour accurately either with standard copper or standard lead solution alone, though some approximate estimate could be formed of the amount of metal present. When copper was kept in solution, however, by addition of potassium cyanide, and the mixture matched by standard lead solution alone (still adding the metal after the introduction of the sulphuretted hydrogen, as in the case of our experiments with single metals), we found in some cases an error amounting to 0.2 c.c. of standard metal solution, or about 20 per cent.

Thus it will be seen that adding the standard metallic solution after the sulphuretted hydrogen to the matching solution in the Nessler cylinder is a method capable of introducing most serious errors into the determination. The nature of the difficulty is apparently indicated by our observation that on using rather stronger solutions than we usually employed, we noticed the production of a minute film of metallic sulphide upon the surface of the liquid as the metallic solution was run in from the burette. This effect is specially noticeable in the case of lead. The production of this film, of course, has the effect of causing more standard metallic solution to be employed than is actually required in any given experiment. For example, in one experiment we recorded an error of 2 c.c. (6 c.c. required in place of 4 c.c.), which equals an experimental error of 50 per cent. of the actual amount of metal present. We also observe that the error increases materially with stronger solutions.

A mixture of lead and copper can be better estimated by employing for com-

parison a lead solution than one of copper, while in this case the addition of potassium cyanide appears to cause too little lead to be used for matching if the metal be added to the solution after the sulphuretted hydrogen. Though in this case the error does not exceed 10 or 20 per cent., yet such an amount seriously impairs accuracy.

It does not appear to make any difference whether lead be compared in acid or alkaline solutions if no other metal be present.

For estimation of mixtures of lead and copper we tried compound matching solutions containing the two metals in equal and other proportions, but found but little success in this direction. Although the difference in colour between the tubes was slight, it was very difficult to judge correctly, while if the proportions of metals are very unequal the difficulty is much increased. If the metal be added before the sulphuretted hydrogen, there is no difficulty in obtaining closely concordant results in the case of copper alone, lead alone, or a mixture of lead and copper. In the case of a mixture of this kind, if potassium cyanide be added to keep up the copper, and the sulphide tint be matched with standard lead, and in a following experiment (on a similar quantity of liquid) an amount of standard lead be first added equal to that used in the first instance, and the difference again matched, using this time standard copper, very accurate results may be obtained, provided always that the metal be added before the addition of sulphuretted hydrogen, otherwise altogether conflicting results are obtained, which are entirely worthless.

It seems to be essential that all experiments with this method must be made under strictly comparable conditions. The same amount of each reagent must be used in each case, and the liquid should be well stirred after each reagent has been added.

The results seem to be most correct when the sample is of the same strength so far as metal is concerned, as the standard metallic solution.

There is a slight error noticeable if much difference exists between the strengths of the solutions, but this error is too small to affect general accuracy of results in practice. If iron be present, it may be prevented from interfering with the tint reactions by the addition of lead-free tartaric acid (as suggested by Dr. Teed).

In those cases where potassium cyanide has also been added to keep the copper in solution, there may be formed a precipitate of Prussian blue if much iron be present. In such an event it would probably be better to estimate the iron by one of the less delicate ordinary volumetric methods.

Thus we have indicated how copper and iron can be practically eliminated from the colour-test and lead estimated in the presence of these metals with considerable accuracy. But in almost every sample of artificial mineral waters, we find that a very notable proportion of tin is discernible. The reason for this and other contamination we shall speak of presently.

We find that by the use of peroxide of hydrogen, tin (if present in small quantities only) can be completely and rapidly oxidized, and will then not perceptibly affect the colorimetric method. But the test must be made rapidly, since after about a minute there is a slight colour perceptible, especially if the amount be somewhat larger than usual; and the colour speedily deepens, and after about five minutes the solution becomes opaque.

An amount of tin that in the stannous condition gives with sulphuretted hydrogen a blackness that makes it impossible to see through two inches of solution, will, if oxidized with peroxide of hydrogen, give, on addition of sulphuretted hydrogen, no more colour than can be matched by less than 0.1 c.c. of standard lead solution. But it becomes opalescent after a very short time.

A standard stannous solution (0.0001 gramme tin per c.c.) may be employed for matching the tint accurately, but this will not keep for more than two days. When tin is present as well as lead or copper, the matching with lead or copper or a mixture of both becomes impossible. Therefore the tin must be prevented from affecting the results in some manner such as we have suggested; otherwise large errors of analysis will arise. It therefore seems to us possible to test accurately, on the lines we have indicated, a complex mixture of the four metals most commonly found in combination. But we find that to give correct and comparable results, all tests must be made under similar conditions. The reagents must be added in the same proportion and same order. The sulphuretted hydrogen solution must be added after the addition of metallic solution in the comparison cylinder, otherwise a scum of sulphide is formed seriously affecting results. It may affect them to the extent of 50 per cent. Also, if the metal be added after the sulphuretted hydrogen, a clear tint cannot readily be obtained, while if the addition be made in the proper order, a clear and readily-matched tint is obtained.

The use of potassium cyanide appears sometimes to give rise to complications, owing to the formation of complex and unstable cyanogen compounds, especially in solutions containing iron. It also seems probable that when a large proportion of copper is present a portion may be precipitated after the addition of potassium cyanide. Possibly this may be due to the formation of a cupro-potassium cyanide in which a portion of the metal is capable of precipitation as sulphide.

Peroxide of hydrogen completely destroys the colour produced by some of the metallic sulphides, even when the tints are very strong. But there is no sharp transition from the oxidation of one sulphide to that of another, though the changes appear to take place in some definite order. Yet the stages are too transient to admit of any satisfactory conclusion being drawn from noting the progress of this reaction, otherwise some valuable information as to the relative proportion of the metallic impurities might possibly have been deduced.

In the case of aerated beverages there is always present a notable amount of carbonic acid gas. It therefore seemed desirable to ascertain if any marked effects were produced upon the tints formed in the reactions employed for determining traces of metallic contamination. Experiments were made, therefore, on this point with rather curious results, which may tend to explain certain anomalies hitherto unaccounted for. The gas was in some instances passed through the solutions before the addition of reagents, and sometimes afterwards. Stated briefly, the experiments hitherto made in this direction show that the iron reactions are most influenced by the presence of carbonic acid; that iron is the only metal affected when the gas is passed first, *i.e.*, before any colour-reaction is produced, and this has an important bearing on the testing of mineral waters. Further, it would seem that copper is never affected by the gas. When the colour reaction has taken place with lead and tin,

the passing of carbonic acid gas causes the sulphides to assume the form of a precipitate.

In a paper of great value read before the Society of Chemical Industry by Mr. R. Warrington, some observations were made on the employment of glycerol in connection with the sulphide tests for lead in tartaric and citric acids. We therefore made a few experiments to judge of the effect of this addition in the case of other metals, and obtained one or two results of interest.

The addition of a small amount (two or three drops) of glycerin partially prevents the formation of a colour or precipitate in the case of all the metals. The employment of 5 c.c. in 50 c.c. of solution does not materially increase this effect, while if a volume of glycerine equal to that of the tested solution be employed, the precipitation is entirely prevented, even in the case of iron, which under the ordinary conditions obtaining in these experiments was found to precipitate most readily. It seems probable that this curious effect of glycerin is due to mechanical rather than chemical causes, but it would seem to indicate the necessity of tests being made in solutions of similar density if really accurate results are desired.

As the result of experiments and observations hitherto made, we deduce the following conclusions :

That it is above all necessary in determination of traces of metals made by these volumetric processes to follow strictly the same order in the addition of reagents, and as closely as possible to employ always the same quantity of reagent, both in the actual experiment and in the preparation of the solution used for the comparative determination.

That all the conditions of experiment must be similar, for example, as to the state of oxidation of the metal, and the presence of extraneous factors affecting reactions, as in the case of carbonic acid gas or substances affecting specific gravity of samples tested. It would seem that, if our results are confirmed, these experiments carry the method of testing for metallic impurities in solution somewhat further than has hitherto been possible, but we are still hopeful of working out a more completely successful process of differential volumetric testing in the case of solutions containing several metals. If this can be accomplished, much facility will be afforded to the analyst who desires to obtain quickly and accurately an estimation of the proportions of metals causing the aggregate metallic contamination of the beverage or solution submitted for examination.

We may observe that in the case of aerated waters and similar beverages artificially prepared, the predominant metal appears in all cases to be tin. We are speaking, of course, of the products of well-appointed manufactories, equipped with modern machinery, and in which only pure acids are employed. Formerly, when it was practically impossible to obtain tartaric and citric acids free from lead, that metal was frequently found in lemonade and ginger-beer, and other acidulated beverages ; while many cases have been recorded, usually from small and imperfectly equipped factories, where a serious amount of lead or copper contamination arose from the use of unsuitable pipes or other appliances. Mr. Stokes showed one of us a sample of ginger-beer from such a source containing a very considerable amount of lead (about 4.5 grains to the gallon). And sometimes contamination has arisen from

the glazing of stoneware bottles and other appliances, such as enamelled metal pans used sometimes for syrup-making. Copper also finds its way from machinery which has not been perfectly coated with some non-injurious material; and there is reason to believe that in some cases, at any rate, a very appreciable amount of copper is dissolved in the aërating cylinders by an electrolytic action set up by the dissolved carbonic acid coming into contact with the tin lining of the vessels and portions of copper exposed by continuous friction. Indeed, we have found a marked increase of copper dissolved when a cylinder has been (by request) allowed to remain filled with carbonated water for an unusually long period. All these points have to be taken into consideration when forming an opinion as to the cause and nature of metallic contamination of beverages. But the most important matter for the analyst is usually to be able to rapidly and accurately estimate the extent of total metallic impurity, and when the quantity is at all considerable, to have a ready method of determining the nature and proportion of the metals severally concerned in producing such total. If these notes tend in any degree to clear the ground in this direction, they will not have unduly occupied the time of the society, we trust.

DISCUSSION.

The Chairman (Mr. O. Hehner) invited discussion on the subject of the paper, and said that he hoped that this would lead to some agreement as to a method for testing water for traces of metallic impurities.

Dr. J. Edmunds referred to the pyrological methods introduced by Colonel Ross, and improved by himself, for the detection and estimation of exceedingly minute quantities of metals. These consisted in reducing a portion of the ash to be examined in a bead of pure boric acid in the flame of the blowpipe, and subsequently examining and measuring the spherule of reduced metal, after the bead had been mounted in Canada balsam, under the microscope. By the use of the filar micrometer, the diameter of the spherules might be taken with great accuracy, and the geometric constants—used with the chemical formula and specific gravity of the substance of the spherule—gave its weight to the millionth of a gramme or even less. A spherule from $\frac{1}{10000}$ to $\frac{1}{100000}$ of an inch in diameter was an easy object to deal with by this method. Copper and lead could be distinctly dealt with in this way, but he (Dr. Edmunds) had not been able to satisfy himself that the method was reliable for tin. Lead and some other metals might be got out on a platinum cathode under the slow action of a couple of Daniell's cells, and then dissolved off and dried up to a residue fit for treatment in boric acid.

Mr. Sidney Harvey thought it was imperatively necessary that the same order should be observed in the comparison of the liquids with the trial test in the case of the estimation of small amounts of metal in solution. That is to say, the reagents must be added in the same order, and in the same amounts.

Dr. Frank L. Teed believed that the amount of lead in a water, when it amounted to one-hundredth of a grain to the gallon, could only be determined by some volumetric process. He had listened with great interest to what Dr. Edmunds had said, but he looked upon his method as a qualitative rather than a quantitative

method of analysis. Mr. Budden's remarks were extremely important, more especially as regards the order in which the solutions were added. In a paper on the same subject Mr. Warington had pointed out that citric and tartaric acids had a specific action on the tint of the lead coloration. He had certainly shown that lead and copper assumed different tints according as they were in presence of water only, or of tartaric, or of citric acid. At the time he (Dr. Teed) was working out his process (on which Mr. Warington's was subsequently based), he was stopped by this obstacle, that there was no pure tartaric, and no pure citric acid to be obtained for love or money. He tested a good many samples, but they invariably contained lead. He suggested in his paper that for the separation of copper, lead, and iron in a natural water, pure tartaric acid should be used, but as he had not got any he could not say that he ever did it. Mr. Warington had proved that citric and tartaric acid affected the colour, and Mr. Budden had shown that carbonic acid also affected it. If it was desired to determine the presence of lead in ginger-beer, he believed the only possible way was to ash it first and get rid of the organic matter. He hoped that Mr. Budden would bring before the society more elaborate notes later on, so that there might be some standard of reference in regard to this subject. In his opinion, when it was a question of .0003 per cent. of lead in a sample, it did not matter whether the result was .0003 or .0004.

Mr. E. J. Bevan did not know whether Dr. Teed made it quite clear to what extent Mr. Warington looked upon the presence of citric acid as the cause of error. He (Mr. Bevan) had had occasion to work on a large number of beverages some time ago, and he had some conversation with Mr. Warington on the subject, and that gentleman informed him of the results he intended to bring forward. He (Mr. Bevan) had found that by adding sugar to the solution the apparent amount of lead was increased as much as ten times. It was necessary, in order to make a satisfactory colorimetric test, that the disturbing constituents should be known, and these must be added to the standard solution. Dr. Teed's course of evaporating down and then igniting would get over that difficulty. It was a remarkable thing that an error of 1,000 per cent. could take place if sugar were present.

Mr. Hehner asked Mr. Budden how he used the peroxide of hydrogen. He understood him to say that turbidity very soon manifested itself.

Mr. Budden replied that he added the peroxide of hydrogen and subsequently the sulphuretted hydrogen water.

Mr. Richmond drew attention to the work of Messrs. Picton and Linder (*Jour. Chem. Soc.*, lxi., 114, 137, and 148), which probably contained the whole explanation of the curious differences observed by Mr. Budden. It seemed to him that variations of colour were due, in some cases, to the formation of different hydro-sulphides. Thus, Messrs. Picton and Linder had obtained with copper hydro-sulphides approximating to the formulæ $7\text{CuS}, \text{H}_2\text{S}$; $9\text{CuS}, \text{H}_2\text{S}$; and $2\text{CuS}, \text{H}_2\text{S}$, of which the first, obtained with excess of sulphuretted hydrogen, was soluble. It seemed to him (Mr. Richmond) that the results of Mr. Warington with citric acid, and those of Mr. Bevan with sugar, were explained by the second and third papers of Messrs. Picton and Linder; they found that different physical modifications show different

colours, and the exact state in which they exist depends partly on the other constituents of the solution. Possibly in these cases the sulphides were more in suspension than they would be with water only as a solvent, and the presence of substances such as citric acid and sugar turned the dissolved body out of solution into a condition of suspension, and thus made the tint appear darker; and therefore in testing for these metals the best thing to do would be to have the conditions most favourable for a state of suspension as against a state of solution—that is to say, this condition should be pushed as far as was compatible with the non-production of actual precipitation, in order to develop the maximum coloration. A study of these papers would be found very interesting.

Mr. Hehner said he believed the statement that citric acid added in quantity would make these sulphides more insoluble was inaccurate. His experience was that citric acid had a contrary effect.

Mr. Richmond admitted that Mr. Hehner's remark, that citric acid prevented complete precipitation of lead sulphide, certainly seemed an apparent contradiction to what he had quoted from Messrs. Picton and Linder's work. But he thought that if their work were read carefully, it would be seen that they had shown that there were so many stages between the actual precipitation and true solution that he (Mr. Richmond) did not think it would be entirely in contradiction. He had also found that lead precipitated as sulphide in presence of citric acid when filtered would run through the filter; but, notwithstanding, though the particles could hardly be seen, the sulphide could be separated from the solution fairly easily, and it certainly was in a state of suspension.

Mr. Bevan asked Mr. Budden what the action of glycerin was; did it keep the lead in solution?

Mr. Budden replied that if there was a certain amount of glycerin added precipitation was prevented, and the matter was kept in solution.

Mr. Hehner thought that the deductions to be drawn from the discussion showed that small quantities of these metals, when mixed together, could be quantitatively determined under certain conditions by colour-tests. When they were in simple aqueous solution there was generally no difficulty; but when it was shown that under other conditions an error might be committed, faith in the colorimetric process was shaken. He had refused to make determinations on very minute quantities of the sample; but he had attempted, with more or less success, by taking a large quantity and evaporating to small bulk, to separate the metals. He imagined that it would be impossible to obtain the metals by incineration. The quantities of sugar and the carbon obtained therefrom were very large. One could not expect to incinerate a milligramme of lead with ten thousand times its weight of sugar without a considerable loss occurring. He would like to ask Mr. Budden whether he had ever used a colorimeter, such as Mills', which would obviate diluting or adding more reagent to the liquid. It was very desirable to arrive at some plan of operation for the future.

Mr. Budden said that the reason which prompted him to bring forward his paper was because he found that some manufacturers of aerated beverages were going the round of the London analysts, and were obtaining results from different chemists

which disagreed with each other, and this seemed to him not only a very unsatisfactory state of affairs, but also one which was not calculated to impress the manufacturers (who wanted to know how they were to get rid of errors in manufacture) with a very high estimate of the methods used by analysts. In regard to ginger-beer, he might say that the metal which generally had to be looked for was lead, and when he could get the beverage sufficiently clear the addition of a trace of acetic acid, and then hydrogen sulphide in solution, enabled the colour to be observed with a certain amount of accuracy. He did not mean to say that it was a perfectly accurate method. The colour produced by ammonia when added to ginger-beer would, of course, necessarily interfere very much with the observations, but he did not see that in some cases it was necessary to have this solution alkalized to that extent. The ammonia appeared to react with some resinous matter in the ginger-beer. The point mentioned by Mr. Bevan interested him exceedingly, because it seemed to be almost the converse of the observation he (Mr. Budden) made about carbonic acid. He had had a case of some dozens of ginger-beer sent to him, all manufactured at one making. After standing some time, the contents of the bottles were found to vary materially in the reactions which they gave, and were also found to vary very materially in the amount of gas present. It seemed obvious that if the amount of effervescence was considerable in any given bottle, there must be a very marked difference in the amount of sugar present. It is very probable, indeed, that the sugar had a marked effect in the same way that glycerine had. He had been making some experiments on a form of colorimeter, and he had had an appliance made which might possibly be useful. It was certainly quite probable that the method might be considerably amplified.
