

A SIMPLE AND EXPEDITIOUS PROCESS FOR THE ESTIMATION OF NITRIC ACID IN WATER ANALYSIS, WITH SOME REMARKS ON THE ESTIMATION OF NITROUS ACID.

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It is well known that when zinc is immersed in copper sulphate solution it becomes covered with a spongy deposit of precipitated copper. If the solution of copper sulphate be sufficiently dilute, this deposit of copper is black in colour and firmly adherent to the zinc. It is, however, not so generally known that the zinc upon which copper has thus been deposited possesses the power of decomposing pure distilled water at the ordinary temperature, and that it is capable of effecting many other decompositions which zinc alone cannot. Among these is the decomposition of nitrates, and the transformation of the nitric acid into ammonia. Messrs. Gladstone and Tribe have shown that the action of the "copper-zinc couple" (as they call the conjoined metals) upon a nitre solution consists in the electrolysis of the nitre, resulting in the liberation of hydrogen and the formation of oxide of zinc. This hydrogen is liberated upon and occluded by the spongy copper, and when thus occluded it is capable of reducing the nitre solution in its vicinity. The nitrate is first reduced to nitrite of potassium, and the nitrous acid is subsequently transformed into ammonia by the further action of the hydrogen. In a paper lately read before the Chemical Society I have shown that even in very dilute solutions of nitre the nitric acid can be completely converted into ammonia in this manner with considerable rapidity; and I have further shown that the reaction may be greatly hastened by taking advantage of the influence of temperature, acids, and certain neutral salts which increase the electrolytic action of the couple. I there showed that carbonic acid—feeble acid as it is—suffices to treble the speed of the reaction, and that traces of sodium chloride (0.1 per cent.) accelerated it nearly as much as carbonic acid. A rise of a few degrees in temperature was also found to hasten the reaction in a very marked degree. The presence of alkalies, alkaline earths, and salts having an alkaline reaction, was found to retard the speed of the reduction.

Upon those experiments I founded a simple and expeditious process for estimating the nitric and nitrous acid in water analysis, which, when used with skill, may be applied to by far the greater number of waters with which the analyst is usually called upon to deal. Before describing this process I will first say a few words upon the nature and use of the copper-zinc couple, about which considerable misapprehension appears to exist even in the best informed quarters. This appears very plainly from the description of the copper-zinc couple process given in the *Handbook of Water Analysis*, recently published by Frankland, in which mistaken directions are given for making the couple and applying it to the estimation of nitric acid in water analysis. There are two kinds of copper-zinc, one (the "dry couple") intended for anhydrous reactions, the other (the "wet couple") intended for hydrogenizations in watery or alcoholic solutions. These two are quite different reagents, differently prepared and different in their application. It is the "wet couple" alone which is adapted to hydrogenizations, such as the transformation of nitric acid into ammonia; but in the handbook

referred to, the dry couple is described as being used for effecting this transformation, a purpose to which I believe it has never been applied, and for which it would certainly be very inefficient.

The wet couple, with which alone we have now to deal, is prepared in the following manner:—The zinc to be employed should be clean, and for the sake of convenience should be in the form of foil or very thin sheet. It should be introduced into a flask or bottle, and covered with a solution of copper sulphate, containing about 3 per cent. of the crystallized salt, which should be allowed to remain upon it until a copious firmly adherent coating of black copper has been deposited. This deposition should not be pushed too far, or the copper will be so easily detached that the couple cannot be washed without impairing its activity. When sufficient copper has been deposited the solution should be poured off, and the conjoined metals washed with distilled water. The wet couple is then ready for use.

To use this couple for the estimation of nitrates, in the manner I am about to describe, it should be made in a wide-mouthed stoppered bottle. After washing it is, of course, soaked with distilled water; to displace this, it is first washed with some of the water to be analysed, and the bottle filled up with a further quantity of the water. The stopper is then inserted, and the bottle allowed to digest in a warm place for a few hours. If the bottle be well filled and stoppered, the temperature may be raised to 30° C., or even higher, without any fear of losing ammonia. The reaction will then proceed very rapidly; but if it be desired to hasten the reaction still more, a little salt should be added (about 0.1 grm. to every 100 c.c.), or if there be any objection to this, the water may have carbonic acid passed through it for a few minutes before it is poured upon the couple. In the case of calcareous waters, the same hastening effect may be obtained, and the lime may at the same time be removed by adding a very little pure oxalic acid to the water before digesting it upon the couple. In my paper communicated to the Chemical Society I showed that nitrous acid always remained in the solution until the reaction was finished. By testing for nitrous acid the completeness of the reaction may be ascertained with certainty, and perhaps the most delicate test for nitrous acid that can be applied for this purpose is that of Peter Griess, in which metaphenylene diamine is the reagent employed. When a solution of this substance is added to a portion of the fluid, and acidified with sulphuric acid, a yellow colouration is produced in about half-an-hour if the least trace of a nitrite be present. The reaction easily detects one part of nitrous acid in ten millions of water. When no nitrous acid is found, the water is poured off the couple into a stoppered bottle, and, if turbid, allowed to subside. A portion of the clear fluid, more or less according to the concentration of the nitrates in the water, is put into a Nessler glass, diluted if necessary, and titrated with Nessler's reagent in the ordinary way.

This process may be used for the majority of ordinary waters—for those that are coloured, and those that contain magnesium or other substances sufficient to interfere with the Nessler reagent, a portion of the fluid poured off the couple should be put into a small retort and distilled with a little pure lime or sodium carbonate, and the titration of the ammonia performed upon the distillates.

About one square decimetre of zinc should be used for every 200 c.c. of a water containing five parts or less of nitric acid in 100,000. A larger proportion should be used with waters richer in nitrates. The couple, after washing, may be used for two or three

waters more. When either carbonic or oxalic or any other acid has been added to the water, a larger proportion of Nessler reagent should be employed in titrating it than it is usual to add. I have found 3 c.c. to 100 of the water sufficient in almost all cases.

In calculating the amount of nitric acid contained in a water from the amount of ammonia obtained in this process, deductions must of course be made for any ammonia pre-existing in the water, as well as for that derived from any nitrous acid present.

To ascertain the amount of nitrous acid in a water, Griess's latest method should be adopted. A one-half per cent. solution of metaphenylene diamine in very dilute sulphuric acid should be prepared, and a dilute sulphuric acid containing one volume of oil of vitriol to two volumes of water. One c.c. of each of these solutions are added to 100 c.c. of the water in a Nessler glass, and the yellow colouration produced (if any) is imitated by means of a standard solution of potassium nitrite with the same reagents. This standard solution is prepared from silver nitrite, prepared by precipitation, and re-crystallized from boiling water. A weighed amount of this pure dry silver nitrite is dissolved in boiling water, decomposed with a slight excess of potassium chloride, and diluted to a convenient strength. The solution I usually employ contains .01 of a milligramme of NO_2 in 1 c.c. A solution of ten times this strength is kept in stock in bottles quite filled and tightly stoppered, and is diluted when required for use. To ensure accurate results the solutions to be compared should be simultaneously started and allowed to stand at least twenty minutes before their tints are compared. They should be at the same temperature, for I have observed that the colouration is developed much more rapidly in warm than in cold solutions. There are other conditions which affect the rate of development of the colouration, but these appear to be of a chemical nature and not easily controlled. In these cases only the final tints of the solution should be regarded. The lengthy time required for the full development of the colour, renders it difficult or at least laborious to prepare a solution of exactly the same tint as that under analysis, and it is therefore desirable to adopt some method of making the titration, which, while sufficiently accurate, shall dispense with the necessity for making a long series of trials. I have usually effected this with the aid of Nessler glasses made from pieces of stout glass tubing, about 30 mm. bore and 200 mm. long, ground at the edges and closed at one end with a glass plate cemented on with Canada balsam. The tubes are of exactly equal bore and are graduated from end to end in millimetres. They are used in the following manner: The solution to be titrated and the test solution are made in the usual way, both columns of fluid being of equal length. The test solution is made as nearly as can be guessed to equal in tint that to be titrated. Usually one will be somewhat deeper than the other; the height of the deeper solution is read off upon the millimetre scale, and a portion of it withdrawn by means of a pipette until the shortened column is equal in tint to the other, when its height is again read off. The amount of nitrite in the shortened column is taken as being equal to that in the other glass, and a simple proportion will give the amount of nitrous acid contained in the solution titrated. In this way the titration can be made very expeditiously.

The metaphenylene diamine solution should be decolourized with animal charcoal whenever necessary.

Dr. Dupré said he was very glad that Mr. Williams had given them the paper and hoped

it would be the forerunner of other papers from other chemists who were not actually members of the Society. With regard to the estimation of nitric acid he had the strongest evidence that the indigo process was absolutely useless when certain kinds of organic matter were present. He was certainly not prepared for its absolute failure, but there was no doubt about it, and they must go to another method. He was very favourably impressed with that described by Mr. Williams, and although it might take a longer time than the indigo process for a single water, yet if a number were to be examined it did not much matter, as after starting the waters something else could be gone on with ; thus the actual work did not take more time than the indigo process, and in many cases would give accurate results where the indigo process would not. He could certainly speak very strongly of the failure of the indigo method in certain waters, and the probability was that it broke down in nearly every case. It broke down entirely in the presence of urine in water, and almost entirely with albumen in water. It was only an approximate method at best.
