ON THE NECESSITY OF STANDARD CONDITIONS IN THE APPLICATION OF WANKLYN'S METHOD OF WATER ANALYSIS.

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The process of water analysis for sanitary purposes, which is commonly known as Wanklyn's method, is still, notwithstanding its admitted imperfections, more commonly used, in English-speaking countries at least, than any other. There is no process of this class which can take its place, and the question of water supply in its sanitary aspects is probably better understood to-day than it could have been without this process. As there is no immediate prospect of a better method, it is desirable that every effort should be made to eliminate its known errors and to so prescribe the conditions of its application that the results obtained by different chemists may be comparable.

By the essential principle of the process organic matter, in alkaline solution, is oxidized by a reagent which constantly varies in strength, and consequently in the temperature at which it acts. If these elements of variation are not the same in successive operations, the results are not strictly comparable. The nature of the organic matter concerned and its susceptibility to oxidation may differ widely in different analyses, and with this difference every condition of concentration, temperature, etc., will vary in its effect, that is, in respect to the quantity of ammonia disengaged in a given time, in a given number of distillates or from a given volume of liquid.

The standards fixed by Wanklyn for interpretation of the results of an analysis are valueless unless all conditions of the analysis be uniform in successive operations. To leave all questions of interpretation, and manipulation as well, to the judgment of the chemist concerned involves so large a personal equation that it may be questioned whether, in such a case, any basis for comparison of results will remain. Decision as to the relative significance of a given quantity of albuminoid ammonia must often be left to the chemist who is familiar with the circumstances under which the water was taken; but the conditions of the analysis should be so clearly defined that no room shall be left for variation in the essential features of the analytical work.

The possible errors of the Wanklyn method relate principally to the rate at which the distillation is conducted and to condensation of the distillate. The general question of loss of ammonia by imperfect condensation, has been quite fully investigated by Dr. Smart (Rep. National [U. S.] Board of Health, 1882). He has also given a few instances in which the time occupied in the collection of each distillate was noted. The writer has reported in a previous paper (this Journal, Vol. VIII., No. 1) a large number of analyses in which the time occupied in collecting each distillate was observed, and he has also called attention to the importance of this feature of the method, and suggested a definite rate as most suitable under the conditions given.

The process as described by Wanklyn takes no account at all of the rate of distillation, and the process is said to be complete when three distillates have been taken off to represent albuminoid ammonia (Wanklyn's Water Analysis, Sixth Edition, p. 40*). The extent to which the distillation is carried is also a matter which should be fixed, since it may happen in the case of dilute solutions that the ammonia evolved sinks below an appreciable amount and then rises again as increased concentration of permanganate and alkali causes more rapid evolution of ammonia.

The loss of ammonia by imperfect condensation which Smart has shown (Rep. Nat. Bd. Health, 1882, p. 251) to average 7.2% in twenty-five experiments, depends both upon time or rate of distillation and temperature of the condenser. It will also depend, although in lesser degree, upon the relative volume of retort and condenser. The loss of ammonia is insignificant when the steam is thoroughly condensed and perfect collection of ammonia requires only a relative abundance of water at a temperature sufficiently low to retain it in solution.

With respect to the possible escape of nitrogen in the form of volatile organic bases, slow distillation offers the best security against such loss by retaining these substances longer in contact with the reagent which will ultimately set free all of the nitrogen which they contain to form ammonia.

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* Subsequently (p. 50), in describing the 100 c.c. method (as a possible substitute for the method using 500 c.c.), he directs that in this case the distillates shall be collected as long as any ammonia can be found in them.

The rate of boiling, or the time occupied in distilling a given quantity of water, being so important, there can be no conformity in results unless some prescribed rate be fixed upon for general use in this process. The writer has found that the rate of ten minutes for each portion of the distillate, when 100 c.c. are taken for analysis, is easily maintained and gives in the aggregate a higher proportionate yield of ammonia than a rate which is somewhat slower. In other words, the yield of albuminoid ammonia does not continue to increase with time of distillation as rapidly above this rate as below it. This limit is found to answer well for many different waters. When 500 c.c. are taken for analysis, and 50 c.c. of distillate collected for each test, the corresponding time is twenty minutes. That the smaller volume should take less time for the evolution of a given proportion of the whole quantity of ammonia contained in it is probably to be explained by the fact that both heating surface of the retort and free surface of the liquid are greater in proportion to volume in the smaller liquid, and these conditions favor, in the latter, the disengagement of ammonia.

The volume of liquid in the retort at the beginning of the analysis, and also when the distillation of albuminoid ammonia is begun, should be the same for the corresponding stages in all analyses; if not, the degree of concentration of the permanganate will be different, and the results will not be comparable. Such discrepancies are largely corrected, it is true, when the distillation is carried nearly to dryness as hereafter directed, but the fact that a larger number of distillates is taken increases, on the other hand, the chance of loss of ammonia by imperfect condensation.

The end of the distillation, or the point at which the collection of albuminoid ammonia is to be stopped, should also be prescribed. The writer prefers the point of approximate dryness as the uniform stopping point in all analyses, and by this is meant the point at which the residue in the retort is reduced to less than the volume of one distillate as measured by the Nessler tubes in use. It is quite safe, either as regards spurting of the liquid or fracture of the retort, to run the liquid down to 5-7 c.c. when 100 c.c. are used, or to 20-35 c.c. when 500 c.c. are taken for analysis, provided that the flame is turned down as the volume of liquid is reduced, and this is necessary at any rate in regulating the time of distillation as above mentioned. Each sample is thus submitted for a long time to the action of the slowly concentrating reagent, and is violently attacked at the last by the same in its strongest and hottest condition. Experience shows that there is always an increased evolution of ammonia at the last with waters that retain any organic matter at all up to this point. To carry the operation further by filling up the retort with ammonia-free distilled water is tedious, and for many reasons impracticable, and it is questionable whether any conclusion can be reached in this way that will permit a closer comparison of waters as to their organic pollution than by the method just given. The quantity of ammonia obtained at each successive refilling is generally very small, and many repetitions may be necessary. Small and frequent additions only can give to the organic matter present a repetition of the conditions obtained at the close of the first distillation, that is, heat and high concentration of the reagent, as all weaker attacks have already been successfully resisted by this matter. Repeated operations also involve, from several sources, an accumulation of small errors, which tends in time to counterbalance the increased accuracy which they aim to secure. The limit of distillation above suggested is a simple and practicable one, it involves no break in the regular course of the distillation, and offers, it is believed, the best approach to uniformity of treatment for all samples of water.

One other point which is closely connected with the foregoing should be fixed as a condition of the process, namely, the preliminary distillation by which the retort is freed from ammonia. Wanklyn's direction to use ordinary water, distilling with alkaline permanganate and then rinsing the retort before introducing the sample, is tedious and unnecessary besides involving much handling of a hot retort. The writer has long used the following method of manipulation which is free from the objections mentioned and has the advantage of being uniform and precise. The retort is rinsed with strong HCl and a fragment of sodium hyposulphite to remove the residue of a previous analysis (or boiled with a mixture of bichromate and sulphuric acid if it be a new retort or one previously used for any other purpose) washed, and rinsed with distilled water. The drawn out neck of the retort enters the tube of the condenser to a depth of at least two inches, and a wide rubber tube, which remains stationary on the condenser, closes the junction as the retort is put in place. A stout ring of rubber (umbrella ring), which slips over the rubber tube, is used to secure the latter upon the neck of the retort when it becomes loose through use. Into the retort are put a few grains of previously ignited pumice,* 2 c.c. of a saturated solution of fused sodium carbonate and 100 c.c. of ordinary distilled water. 85 c.c. are distilled off rapidly into a flask holding that volume to a mark on the neck, and 10 c.c. into a Nessler tube, the latter being tested for ammonia. The residue in the retort should then be from 4 to 7 c.c. This preliminary operation furnishes, incidentally, a good test of the condensation. The retort being shown to be free from ammonia, 100 c.c. of the water to be tested is introduced and distilled to approximate dryness under the conditions hereafter given. The possible objection to the procedure just given is that the residue of the distilled water may contribute something to disturb the result. As to this it is plain that free ammonia is out of the question and the absence of albuminoid ammonia can be shown by an occasional analysis in blank, remembering in this case that any trace of albuminoid ammonia obtained represents twice what would occur in an analysis, as two portions of 100 c.c. each will be used. In practice, if distilled water be free from sediment and dust, no disturbance of the analysis is to be feared from this source. The above directions apply to the use of 100 c.c. for analysis. If the older, or 500 c.c. method, be preferred the quantities are proportionally increased except that 200 c.c. of water suffice for the preliminary operation.

The use of 100 c.c. instead of 500 c.c. was recommended by Wanklyn long ago and the same directions appear in later editions of his water analysis. It is much to be regretted that its use has not become general to the exclusion of the older (500 c.c.) method. It is at once more simple, more accurate and more economical of time and material than the latter. It is evident that the estimation of a given weight of ammonia by the Nessler test in a column of liquid 10 c.m. in depth for a volume of 10 c.c. must be

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* This pumice is prepared in quantity by breaking it, and sorting to a size of $\frac{1}{8}$ inch, free from dust. It is ignited for ten minutes at a red heat, in a platinum dish, and kept in a tightly stoppered, wide mouth bottle.

more accurate than the estimation of five times that weight in a column of 15 c.m. in depth for a volume of 50 c.c. In practice it is less difficult to detect .0005 of ammonia in a 10 c.c. tube than .005 of ammonia in a 50 c.c. tube. The smaller tubes, moreover, are more convenient to handle, less liable to break and far less costly. Not the least advantage of the 100 c.c. method is the saving which it effects in the use of that peculiar reagent—troublesome to prepare and difficult to keep—ammonia-free water. The testimony of chemists who have tried both methods is entirely in favor of the smaller volume. The writer has used the 100 c.c. method in more than five hundred analyses.

With regard to the plan of distilling to approximate dryness in the determination of albuminoid ammonia, it may be asked whether results obtained in this way are in any sense comparable with those obtained by following Wanklyn's directions. These directions, as has already been said, are misleading so far as the 500 c.c. method is concerned, and results obtained by them will not be comparable among themselves. To distil to the point at which the evolution of ammonia appears to cease, may also be misleading in some cases, unless that point corresponds with great reduction of volume of liquid in the retort. The proposed method yields results which compare much better among themselves, and quite as well with the latter in general, as these latter compare with one another. The writer has found from a study of twenty-four analyses that the yield of albuminoid ammonia (from Croton water) between the third distillate and the point of approximate dryness was, on an average, one-third of that yielded in the first three distillates. The required correction would be much less than this amount where the distillation was carried to entire disappearance of ammonia, as is commonly done.

The modifications of the Wanklyn process suggested above may be summarized in the following plan, by which it is believed that many of the uncertainties of that process may be eliminated.

1st. Into a glass stoppered, half litre retort put 100 c.c. of distilled water, 2 c.c. of saturated solution of fused sodium carbonate and a few fragments of previously ignited pumice.* Distil off rapidly 85 c.c. into a flask, and reject; collect the following 10 c.c. and nesslerize.

2d. Add 100 c.c. of the water to be tested, collect 4 portions of 10 c.c. each for free ammonia and nesslerize each. Each distillate should be allowed ten minutes to collect.

3d. Put 11 c.c. of alkaline permanganate* solution into a small beaker, having a file mark on its side, representing 16 c.c., and another mark for 11 c.c. Add ammonia-free water to the upper mark, and boil down to the lower mark ; then transfer the hot liquid through a long-necked funnel to the retort. Distil off seven portions, allowing 10 minutes for each distillate, and lowering the flame occasionally as the volume of liquid is reduced. The operation is then finished, and 4-7 c.c. should remain in the retort.

The weak standard solution of ammonia and the Nessler reagent are delivered respectively from glass stoppered burettes, one measuring to $\frac{1}{20}$ (.05) c.c., the other to $\frac{1}{2}$ c.c.

The directions apply equally well to the 500 c.c. method except, as already stated, that 200 c.c. only of water are used for the preliminary distillation and that twenty minutes instead of ten are given to the collection of each distillate.

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* The alkaline permanganate solution is made with ordinary distilled water, and is boiled down in preparation from 1500 c.c. to one litre, 500 c.c. of water in excess being added at first. The volume of 11 c.c. is used in order that 1 c.c. may be allowed for drainage, etc. The volume quickly delivered into the retort is then little over 10 c.c. This portion is prepared during the collection of free ammonia, and the distillation is only interrupted for a moment in introducing it.