On applying to this process the data obtained by Duclaux* we find that the distillation of 50 c. c. from a total of 70 c. c. should give over 80 per cent. of the butyric acid present in the first distillate, and that three distillations conducted in this manner should give practically all. Duclaux found, however, that the presence of glycerol slightly diminishes the proportion of acid distilled over. In this case we have glycerol present, as well as much potassium sulphate, which may exert some influence by making the boiling point of the liquid higher. It is difficult, therefore, to say whether by following up this plan of action we may eventually be able to determine the proportions of the different volatile acids with ease and certainty. The idea, however, looks promising.

ON THE EXAMINATION OF CROTON WATER.

By A. A. Breneman, S. B.

The analyses of Croton water presented by Dr. Waller cover the period in which my own analyses of the same water were made. (This journal Vol. III., 1), but the differences between our results are so marked as to call for further discussion. Through the kindness of Dr Waller I have had a copy of his paper in time to discuss it at this meeting. The following tables contain some of the results in question, single analyses being compared only when they relate to samples taken on the same day. There were no analyses of the same date during October, November and December, and a comparison of monthly averages is therefore added. As the question at issue relates entirely to albuminoid ammonia all other items are omitted.

ALBUMINOID AMMONIA IN CROTON WATER—PARTS PER 100,000.

Daily Analyses.

Date.	W.	B.	Diff.
1885.			
May 6	.0166	.0217	.0051
" 26	.0086	.0192	.0116
June 13	.0070	.0190	.0120
" 30	.0140	.0213	.0073
July 15	.0080	.0246	.0166
" 30	.0110	.0211	.0101
Aug. 19	.0140	.0228	.0088

* Ann. Chem. Phys. [5], II., 233.

Averages per Month.

Date.	W.	B.	Diff.	No. of Analyses.	
				W.	B.
1885.					
May	.0126	.0195	.0069	2	20
June	.0105	.0188	.0083	2	25
July	.0095	.0227	.0132	2	24
Aug	.0115	.0252	.0137	2	24
Sept	.0127	.0269	.0142	2	10
Oct	.0140	.0162	.0022	2	6
Nov	.0140	.0160	.0020	1	3
Dec		.0162		0	4

Such differences as these are beyond any reasonable limit of error. They point to defects in manipulation upon one side or the other which must be inquired into before a conclusion as to the true state of Croton water can be reached.

The comparisons between seven pairs of analyses representing waters taken on the same day indicate also that the differences are inherent in the methods used.

The monthly averages of Dr. Waller's analyses lead to the rather startling conclusion that the water contains on the whole less nitrogenous organic matter in summer than in autumn. My own analyses (*loc. cit.*) show, on the contrary, a slow general rise in albuminoid ammonia with the advance of summer, a maximum in the early part of September, and a somewhat rapid decline thereafter, coinciding in general with the fall in temperature. Other considerations apart, there is a value in the accordance of more than one hundred analyses upon this point as compared with the small number embraced in Dr. Waller's list. For the rest the belief that Croton water is better in summer than in autumn is not sustained by experience or reason. The most active growth of low animal and vegetable life is known to coincide with the annual rise in temperature and the abundance of visible and microscopic representative of such life, and of the debris resulting from it, shows how large a factor it is in the organic contamination of this water.

The suggestion that the difference of locality in the city from which the samples were taken may account for differences in the analyses seems to me untenable. If such differences existed in the quality of the water in the mains in different parts of the city at a

given time, it is inevitable that they would lead to analytical errors of opposite character at different times, whereas the differences in these analyses are uniformly in the same direction.

Again, if the differences in question were due, as Dr. Waller suggests to some form of nitrogenous matter present in Croton water in summer, but disappearing at the approach of frost, there would be in this only an additional condemnation of his method, since there must then be a large part of the year—and that the most dangerous in respect to impure water—in which chemical methods fail to indicate the presence of a large proportion of the matter which is believed to stand in close relation to the healthfulness of the water. It is quite possible that there is nitrogenous matter, difficult of oxidation and therefore requiring prolonged action of the alkaline permanganate, in Croton water during summer, but such matter is putrescible like the rest, and should not escape decomposition in any effective process of water analysis. In the absence of any direct evidence upon this point, I venture the suggestion that it is animal and vegetable matter *living* at the time of introduction into the retort, which thus resists oxidation, and which has escaped detection in Dr. Waller's analyses. Later in the season such matter is replaced in great part by the debris resulting from its death and decomposition, and this latter is more readily acted upon during rapid distillation or in a highly dilute solution of alkaline permanganate.

The procedure described by Dr. Waller in his application of the Wanklyn process is open to several objections and in these will be found, I believe, the explanation of the low figxres he obtains for albuminoid ammonia. The process, as he describes it, begins by putting "250 to 500 c.c. of some water (usually Croton)" into the retort for the preliminary distillation. This want of constancy in volume is of itself a source of error; the same volume of water should be introduced in every case or at least it should be reduced to a constant volume at the time when the sample for analysis is put into the ammonia-free retort, which latter does not seem to be the case in Dr. Waller's manipulation. As the volume of liquid is different in different analyses, at the same stage of the distillation, as a consequence of the above procedure, the alkaline permangarate is of different degrees of strength and the activity of oxidation must also be different. The results therefore are not strictly

comparable even in dealing with water from the same source. Also the large volume, which must much exceed 500 c.c. in some cases at the beginning of an analysis, is an obstacle to the evolution of ammonia, since for equal weights of ammonia in solution, complete disengagement by boiling requires a longer time as the volume of liquid is greater. This leads to the consideration of a question of the utmost importance to which I have referred in a previous paper (*loc. cit*), namely the *time* occupied in taking off the albuminoid ammonia. Dr. Waller has given no details upon this point. As the action of the permanganate and the disengagement of ammonia are both affected by the time occupied in the distillation it is quite possible by rapid distillation to obtain results uniformly low in proportion to the amount of albuminoid matter present. In practice the most various results may be obtained by varying the duration of the distillation for albuminoid ammonia, especially if the distillation be stopped at an early stage as it would be with rapid distillation because of the apparent absence of ammonia in the distillate. In the latter case the advantage of concentration of permanganate at a later stage, which would counteract to a great extent the evil of rapid distillation, is lost. It is probable that the attack of alkaline permanganate upon the solid particles which represent the bulk of the albuminoids in Croton water goes on principally upon the surface, and new surfaces are exposed only by the disintegration and solution of the outer layers. Oxidation will therefore be proportional to time, until the volume of liquid is greatly reduced, after which the great increase in strength of the reagent determines, in waters of this class, a more rapid oxidation, and, as experience shows, a somewhat abrupt increase in the evolution of ammonia when the liquid is low in the retort.

The conditions of large volume and rapid distillation are all that are necessary therefore to account for the low results obtained by Dr. Waller. The first condition is admitted and the second is, to some extent, a consequence of the first.

My own results were obtained as already stated (*loc. cit.*) by regulating the time of distillation so as to occupy ten minutes for each distillation, and by running the liquid down to almost dryness in the retort. As there is no point short of approximate dryness at which Croton water ceases to yield a distillate containing a measurable quantity of ammonia when distilled in this way,

any stopping-point short of this is purely arbitrary, and it is questionable whether it is safe to introduce such an arbitrary condition into a general method. I have, however, suggested provisionally (*loc. cit.*) that a deduction of one-fourth of the total albuminoid ammonia found in this way be made, in order to render the results comparable with those obtained by Wanklyn's method of stopping the operation after the collection of the third distillate. The correction, however, is hardly applicable to Dr. Waller's results, as he stops his distillation only with the (apparent) disappearance of ammonia. Admitting this correction however, for the sake of argument, the differences in the results shown by the table are still too large to be passed over.

The question of chlorine to which Dr. Waller alludes, relates to a proportion never exceeding 0.3 grains per U. S. gallon, but I willingly concede that the evaporation of a litre of water for the chlorine test, will secure greater accuracy than direct titration. The only point to consider is, whether the gain, in the case of so small a quantity of chlorine, is of any practical importance.

As to the possible influence of imperfectly prepared alkaline permanganate in increasing the albuminoid ammonia, I can only say that is my custom to prepare the reagent by prolonged boiling and to boil again for ten minutes before putting it into the retort. It is inconceivable that any albuminoid matter present in the alkaline permanganate itself which could resist such action of a concentrated reagent should afterwards yield to the same reagent in much more dilute form in the retort.*

* Since the reading of this paper, the writer has made seven analyses by the Wanklyn method, *in blank*, using distilled water as the sample for analysis. The yield of albuminoid ammonia, per 100,000, was as follows, viz., maximum, .0027,—minimum .00035,—mean .00158. As the quantities of albuminoid ammonia found cover the aggregated, positive errors of the process, only a small portion, if any, being chargeable to the alkaline permanganate, it is evident that errors from this source may be neglected.