

## IMPROVED METHODS OF WATER ANALYSIS.

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WE have in the South Atlantic States incontestable evidence that the true source of malarial disturbance is to be found in the water, and not in the air, as was formerly supposed. The introduction of deep-seated artesian wells has very materially decreased this trouble, and has rendered localities that were notoriously unhealthy, perfectly healthy.

The examination into the exact difference between the malaria-producing waters and those proof against it, has had the writer's attention for over two years, and the work herein detailed is a portion of the preliminary work looking into the best methods of analysis.

My experience with the Wanklyn process as ordinarily carried out with the usual apparatus, so impressed me with its crudeness, that for a long time I have had little confidence in the results I obtained. The loss by imperfect condensation, the crude way of adding the permanganate solutions, and the open-air contamination of the distillate are by no means in keeping with accurate work. The loss by imperfect condensation is very much greater than we permit ourselves to believe, and with the original Wanklyn process<sup>1</sup> is a very difficult matter to control; the loss is variable, and is dependent upon the rate of distillation and the efficiency of the cooling apparatus. After making a long series of experiments upon every character of material liable to be found in water, I am satisfied that a rate exceeding fifty cc. in fifteen minutes is accompanied by loss. As a modification of the Wanklyn process, Mallet<sup>2</sup> proposes to keep the original volume of liquid in the retort constant by the systematic addition of ammonia-free, distilled water, in order to prolong the action of the permanganate; this is objectionable, inasmuch as the operation is endangered by a constant source of error in the addition of ammonia-free water, which is difficult to obtain in so large a quantity.

<sup>1</sup> Wanklyn and Chapman Water Analysis. (6th ed.). 1887, pp. 38-40.

<sup>2</sup> Report National Board of Health. 1882, p. 210.

In my own work I had frequently noticed that the evolution of ammonia very often increased as the liquid in the retort became more concentrated.

Acting on this observation it occurred to me that by the action on a smaller and limited quantity of water by the full strength of the permanganate solution and supplying the water under examination at about the rate of distillation, very much better results could be obtained ; this I have now confirmed by a great many comparative analyses.

The apparatus used is shown in Fig. 1, and consists of distillation flask A, of one liter capacity, into which is fitted by a ground joint the remainder of the apparatus (this is the only

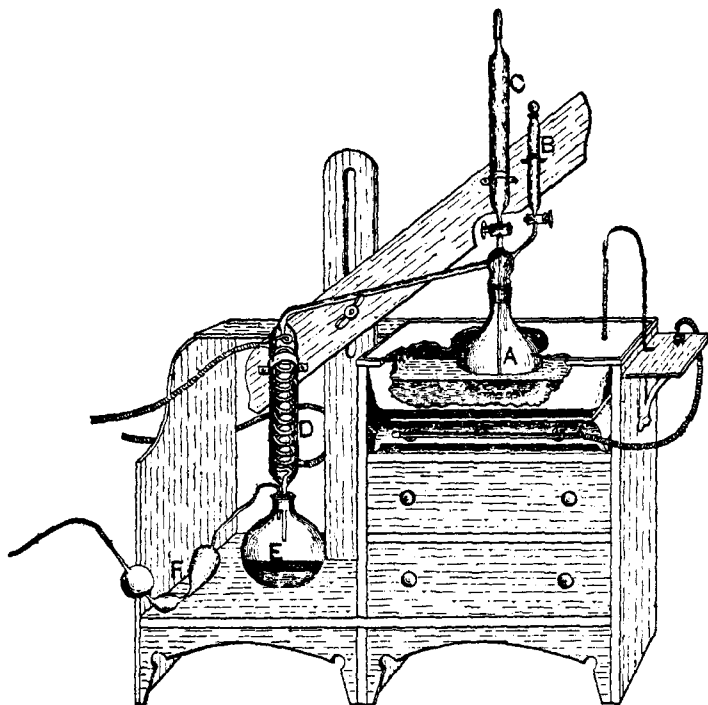


FIG. 1.

connection the apparatus has); through the bulb of the neck we have two burettes with stop-cocks, the smaller, B, with a capacity of fifty cc., with its tube projecting within three inches

of the bottom of the distillation flask; the larger burette C, has a capacity of 250 cc. and its tube projects to within one-half inch of the bottom. The cooling apparatus D, is a closely coiled glass worm, with a long projection at the lower extremity, to which is attached the distillate vessel E, by a soft rubber stopper, which also has tube for connection with the Will and Varrentrapp absorption bulb.

The apparatus is constructed to work under greatly reduced pressure, and the connection with distillation flask, as well as the stop-cocks, are accurately ground to remain tight without a lubricant.

The apparatus is mounted as shown, raised and lowered into the bath by means of a thumb-screw, as indicated. The whole is very easily managed, and is very serviceable. I have made over a thousand determinations with mine, and there is no reason why it will not continue to do good service for a very long time to come.

The heating of the apparatus is effected by setting the flask into a fixed saline-bath, with a covered top as shown, and heated from below by a two-pipe gas-burner.

*Mode of Procedure.*—After thoroughly rinsing the apparatus with ammonia-free distilled water, 500 cc. of the water under examination are put into the flask and the apparatus connected and lowered into the bath, the distillate flask with Will and Varrentrapp bulb, the latter previously charged with Nessler solution, are now attached and connected with the pump.<sup>1</sup> The partial vacuum is now established gradually, the sodium carbonate solution added by way of the smaller burette, and the distillation started and continued until 200 cc. have been distilled over, which is then nesslerized for free ammonia.

The vacuum tube is now disengaged and the stop-cock on large burette opened and about 250 cc. of the liquid in the distillation flask drawn up and the fifty cc. of alkaline permanganate solution, previously poured into the smaller tube, is now allowed to run in after the distillate flask has again been attached.

<sup>1</sup> Richards is an excellent device, but it is important to have a small check-valve in the tube to prevent the water being drawn into the apparatus when the water pressure is suddenly diminished. A very simple valve is made of oiled silk opening only toward the pump.

We now have fifty cc. of alkaline permanganate acting on fifty cc. of water, and after, say thirty to forty cc. have been distilled over, the water in the large tube is allowed to drop in at the same rate as the distillation, which must not exceed fifty cc. in fifteen minutes. [The rate of distillation, as recommended by the Chemical Section of the American Association for the Advancement of Science, *i. e.*, fifty cc. in ten minutes, is too rapid, and is very frequently accompanied by loss by imperfect condensation; this is very readily observed in my apparatus by discoloration of the Nessler solution in bulb.] The distillation is continued until 250 to 300 cc. have been distilled over, which is then nesslerized.

The following notes from my laboratory work will show the general plan of the work :

One gram urea was *dissolved in one liter* ammonia-free water.

1. Ten mgms. urea in 300 cc. of ammonia-free water, 250 cc. drawn up into tube, fifty cc. permanganate solution added, bath  $87^{\circ}$  C., cooling water  $28^{\circ}$  C., pressure six and a half inches, distillation at rate of 150 cc. per hour, 310 cc. distilled over with slight discoloration of Nessler bulb.  $30.2 : 2.0 :: 310 : 2.053$  mgms. ammonia, or 20.53 per cent. which is 36.2 per cent. on ammonia obtainable.

2. Five mgms. urea in 300 cc. ammonia-free water treated as above—297.4 cc. distilled over, no discoloration of Nessler bulb.  $28.8 : 1.0 :: 297.4 : 1.032$  mgms. ammonia, or 20.64 per cent. which is 36.4 per cent. on ammonia obtainable.

3. Ten mgms. urea in 300 cc. water, 250 drawn up, fifty cc. permanganate solution added, bath  $85^{\circ}$  C., cooling water  $27^{\circ}$  C., pressure five inches, rate of distillation, 100 cc. per hour, 290 cc. distilled over, no discoloration of Nessler bulb.

$25.1 : 2.0 :: 290.0 : 2.310$  mgms. ammonia, or 23.10 per cent. on 40.7 per cent. on ammonia obtainable.

4. Ten mgms. urea in 500 cc. water, ten cc. strong solution sodium carbonate added, bath  $87^{\circ}$  C., cooling water  $28^{\circ}$  C., pressure five and a half inches.

210 cc. distilled over as free ammonia, which yielded 0.835 mgms. ammonia or 8.35 per cent.

250 cc. were then drawn up, fifty cc. permanganate solution added, and distilled as before.

305 cc. were distilled over, which yielded 2.296 mgms. ammonia, or 22.96 per cent.

Total ammonia 8.35 per cent. free, plus 22.96 per cent. albuminoid, or 31.31 per cent. which is 55.2 per cent. on ammonia obtainable.

Rosaniline hydrochlorate yielded	86.02	per cent.	on ammonia obtainable.
Strychnine sulphate	" 78.10	" "	" "
Urea-boiling five hours	" 79.90	" "	" "
Cyanuric acid	" 61.10	" "	" "
Quinine sulphate	" 77.09	" "	" "
Morphine sulphate	" 81.11	" "	" "

The apparatus, Fig. 1, is also used for the Kjeldahl process. This process was first described for use in general water analysis by Drown and Martin,<sup>1</sup> and is now very generally used in place of the Wanklyn process.

I have modified the Kjeldahl process so as to insure more perfect decomposition, and have obtained most gratifying results with the most obstinate organic compounds.

*Process.*—300 cc. of the water under examination is put into the distillation flask of apparatus already described (Fig. 1) and the whole connected up; ten cc. specially prepared concentrated sulphuric acid is allowed to drop in slowly by way of the smaller burette, the whole is then allowed to digest at 85° C., under diminished pressure for, say one hour, and then brought to a boil, and so continued until the contents are colorless. The acid is then neutralized and the solution rendered strongly alkaline by the addition of fifty cc. strong solution of ammonia-free, sodium hydroxide through the smaller tube.

250 cc. of the contents are then drawn up into the larger tube and fifty cc. of permanganate solution added through the smaller tube, and the distillation carried on as already described in the modifications of the Wanklyn process, and nesslerized as before.

The modified process combines the good features of the Wanklyn and Kjeldahl, and is easily carried out with the apparatus described. The original sources of error are now practically eliminated.

The following are some results upon some of the substances

<sup>1</sup> Technology Quarterly, 2, 3.

that with the Wanklyn process yield only a very small percentage of the ammonia. I have made no comparative tests with the original Wanklyn process, and quote Mallet's:<sup>1</sup>

Mine.	Mallet, by Wanklyn's Process.
Rosaniline hydrochlorate 96.9 per cent.	23.8 per cent of theoretical amount.
<sup>2</sup> Cyanuric acid (distillation two hours) 89.1	2.1
Cyanuric acid (distillation four hours) 91.2	
Urea (from urine)..... 100.3	22.2
Urea (from ammonium cyanate)..... 99.0	20.8
Potassium ferrocyanide 59.8	none

In nesslerizing I have found the Leed's Comparator modified as in Fig. 2, best suited to my wants. The work is very much facilitated by having one tube with stop-cock carefully graduated up to 100 cc., and connected to another tube, as shown in Fig. 2 ;

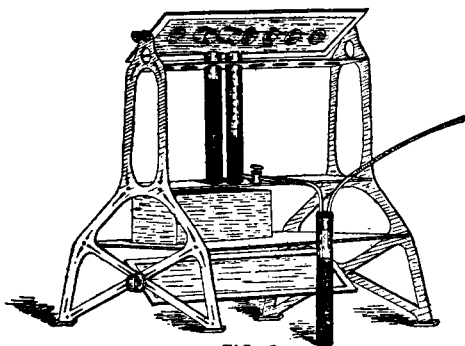


FIG. 2.

by using the blowing tube the liquid can be raised or lowered at will, and compared with the known solution with a nicety and exactness that I have been unable to attain by any other plan.

*Combustion Process.*—The Frankland combustion process<sup>3</sup> is entitled to more general use for regular work on water analysis; in my hands it has yielded satisfactory results after eliminating the objectionable features of open-air evaporation.

<sup>1</sup> Report Board of Health, page 253-254.

<sup>2</sup> After standing over night yielded 1.7 per cent. additional.

<sup>3</sup> Frankland: Water Analysis, London, 1850.

The apparatus designed for this purpose is shown in Fig. 3, and is constructed to hold a vacuum of fifteen mm. for four hours after pump has been stopped. The vessel A is set into a fixed table water-bath, to a depth of two inches, and the water under examination, in closed reservoir, B, the capacity of which is 200 cc., is admitted into A by a tube of very fine bore, and the vapor of water carried over into the sulphuric acid absorption col-

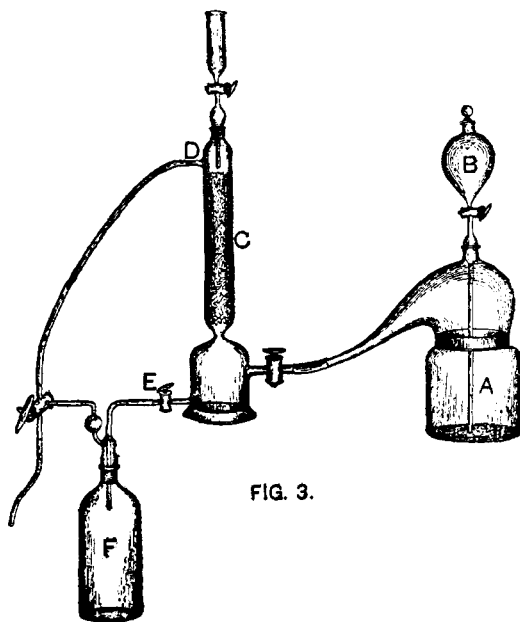


FIG. 3.

umn C, which is filled with broken glass tubing and has travelling through it, pure concentrated sulphuric acid. The vacuum tube to jet-pump is connected to the upper, D, and lower, E, connection of the absorption column by a three-way cock, by which the operation is momentarily suspended and the vacuum held, while the acid accumulated in the lower part of the column is drawn into a bottle, F, by diminished pressure.

Concentrated sulphuric acid is such a powerful absorbent that under the vacuum produced by a good jet-pump, ice can be readily and rapidly formed in the vessel, so that with the water in the bath at  $30^{\circ}$  C., the evaporation is rapid; actual boiling,

however, must not be permitted. The water is admitted only at the rate of evaporation which can be adjusted to a nicety by the stop-cock. Care must be taken to start the pump cautiously, thereby establishing the vacuum gradually, and to have only a thin layer of water in the vessel to avoid serious spattering in the escape of the bubbles of gas. In this way 500 cc. of water is evaporated to dryness in six to seven hours, and requires little or no attention after the apparatus is once adjusted.

The following comparative experiments have been made on water:

	PARTS PER MILLION.			
	Wanklyn.	Wanklyn with my modifications and apparatus.	Kjeldahl, Drown, and Martin.	Kjeldahl with my modifications and apparatus.
	Free and albuminoid ammonia.		Organic nitrogen calculated as ammonia.	
Savannah river at } Augusta . . . . . }	Free, 0.011	Free, 0.010	0.172	0.175
	Albu., 0.130	Albu., 0.165		
	0.141	0.175		
Savannah river, at } 26 feet. . . . . }	Free, 0.180	Free, 0.183	0.421	0.420
	Albu., 0.135	Albu., 0.236		
	0.315	0.419		
Well water, Sum- } merville . . . . . }	Free, 0.092	Free, 0.105	0.285	0.287
	Albu., 0.116	Albu., 0.186		
	0.208	0.291		
Spring water sup- } plying Hotel Bon } Air . . . . . }	Free, 0.015	Free, 0.018	0.205	0.219
	Albu., 0.123	Albu., 0.209		
	0.138	0.227		
Driven well, be- } low Augusta . . }	Free, 0.685	Free, 0.700	1.855	1.867
	Albu., 0.605	Albu., 0.976		
	1.290	1.676		
Driven well in So. } Carolina . . . . }	Free, 0.416	Free, 0.422	1.116	1.121
	Albu., 0.395	Albu., 0.566		
	0.811	0.988		
Artesian well } water, Georgia } Chem. Works.. }	Free, 0.005	Free, 0.005	0.050	0.050
	Albu., 0.036	Albu., 0.042		
	0.041	0.047		
Distilled water } with 10 per cent. } of water from pool } in garbage pile.. }	Free, 0.620	Free, 0.653	3.007	3.100
	Albu., 1.136	Albu., 2.251		
	1.756	2.904		

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