Discussion.—Dr. Wiley.   By our organization we are able to present to American chemists the latest and most accurate numbers for atomic weights.   It is a matter for congratulation that this has been accomplished by the American Chemical Society.

UPON THE DETERMINATION OF NITRATES IN POTABLE WATER.

BY AUGUSTUS H. GILL.
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PART II.

(b) THE REDUCTION TO AMMONIA.

AFTER a discussion of the various processes for the determination of nitrates by reduction to ammonia, Tiemann concludes with the following :[1] "On account of the unreliability and chances for error which this principle involves, we strongly advise against its use."[2]   Tables are given, pp. 208 *et. seq.*, in which the results obtained by reduction with sodium amalgam, aluminum, and the zinc-copper couple, vary from plus ten to minus thirty-eight per cent. which sufficiently illustrate the unreliability.

The objections to any method for such reduction are in brief :

1. THE NUMEROUS CORRECTIONS TO BE APPLIED :
   - I.   For free ammonia.
   - II.   For nitrates.
   - III.   For materials used.
   - IV.   For ammonia carried away by the hydrogen.

2.   The liability of reducing the organic matter present in the water to ammonia.

3.   The time required and chances for error in manipulation.

To the method proposed by Hazen and Clark,[3] they not distilling the reduced liquid before nesslerizing are added two more, *viz.* :

4.   The colors produced by the Nessler reagent are in many cases not the same *tone* as the standards, and are usually read higher than the amount of ammonia actually found by distilla-

1 "*Die chem. und bacteriologische Untersuchung des Wassers.*" Tiemann und Gaertner Braunschweig *1890.* 212.

2 " Entschieden davon abzurathen."

3 *J. Anal. Appl. Chem.,* 5. 3.

tion;[1] see Nos. 2, 3, and 20 in the following table.

5.   When the reduction is finished the liquid in the Nessler tube is not homogeneous, hence the removal of a portion with-out mixing—which at the same time occasions a troublesome turbidity—does not represent the amount of ammonia actually present.

All these objections might well be waived did the method yield reliable results; but as is shown in the accompanying tables, it is s bject to even greater variations than the phenolsulphonic acid process.

RESULTS OF THE ESTIMATION OF NITRATES IN WELL WATERS BY THE ALUMINUM AND PHENOLSULPHONIC ACID METHODS.

PARTS OF NITROGEN IN 100,000.

No.	P. S. A.	Aluminum direct.	crosswise.	distilled.	Differences From P. S. A.	Per cent.	Nitrites.	Chlorine.
1..	0.4000	0.4323	.....	.....	+0.0323	7	none	2.93
2*.	1.1500 {	1.0287 }	.....	0.9876	{ −0.1213	{ 10	0.0001	2.78
		0.8306 }	0.7407	.....	{ −0.2194	{ 23		
3*.	1.0000 {	0.8306 }	{ 0.7407 }	.....	{ −0.1694	{ 17	}	2.22
		0.8235 }	{ 0.6995 }	0.7407	{ −0.1765	{ 17		
4..	0.9000	0.8235	.....	.....	−0.0765	8		2.16
5..	0.0090	0.0041	.....	.....	−0.0049	50		0.34
6..	0.0085	0.0041	.....	.....	−0.0044	50		0.29
7..	0.0500	0.0625	.....	.....	+0.0125	40		0.75
8..	0.4500 {	0.3045 }	.....	.....	−0.1455	{ 33		0.96
		0.3538 }	.....	.....	−0.0962	{ 20		
9..	0.0060 {	0.0288 }	.....	.....	+0.0228 }	{ 400	none	0.35
		0.0000 }	.....	.....	−0.0060 }	{ 100		
10..	0.0140 {	0.0329 }	.....	....	+0.0189	{ 120		0.34
		0.0513 }	.....	.....	+0.0373	{ 250		
11..	0.4200	0.3538	.....	.....	−0.0662	15		0.91
12..	0.0000	0.0000	.....	.....	.....	..		0.66
		0.0000						
13..	0.0400	0.0411	.....	.....	+0.0011	2		0.54
14..	0.3250	0.2472	.....	.....	−0.0778	21	}	1.12
15..	0.7000	0.7242	0.6172	.....	+0.0242	3	0.0001	3.40
16..	0.7200	0.6748	.....	.....	−0.0452	5	0.0003	2.40
17..	0.2500	0.2634	.....	.....	+0.0134	5	0.0002	2.57
18..	0.3000	0.3127	0.2469	.....	+0.0127	4	0.0005	2.42
19..	1.0000	1.0287	.....	.....	+0.0287	3	0.0000	+.60
20*.	1.6000 {	1.3414 }	1.1522	.....	−0.2500	15	0.0002	2.42
		1.4418 }						
		1.3579 }	1.2345	1.3168				

[1] The reason for the difference in tone of the reduced solutions is probably due to the presence of hydroxylamine, as the colors produced can be closely imitated by solutions of this compound. This is unaffected by the excess of alkali, and is with difficulty reduced to ammonia; upon distillation it breaks up into ammonia and nitrogen, thus giving rise to a loss of the latter.

$$3NH_2OH = NH_3 + N_2 + 3H_2O$$
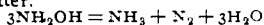
By "crosswise" is meant the comparison of the tubes when looked through diametrically instead of axially as is customary ; this was done, as the colors were not the same tone, to see if they could be matched more closely; the· "distilled" column indicates the results as obtained by distilling a portion of the reduced. liquid in addition to nesslerizing directly, it will be observed that these results are *lower* than those obtained by direct reading.

The method is supposed to be particularly valuable in the presence of relatively large amounts of chlorine ; of eleven waters there given having a higher percentage than one part per hundred thousand, *five*, Nos. 1, 15, 17, 18, and 19, are estimated from 3–7 per cent. *higher* and *six*, Nos. 2, 3, 4, 14, 16, and 20, are estimated from 8–20 per cent. *lower* than the results of the phenolsulphonic acid process. Of the remaining waters three are estimated much too high and four as much too low.

Let us consider another table, this time of solutions made to contain definite quantities of nitrate ; each letter represents a different and independent observer.

RESULTS OF THE DETERMINATION OF NITRATES IN STANDARD
SOLUTIONS BY THE ALUMINUM AND PHENOL-
SULPHONIC ACID METHODS.

PARTS OF NITROGEN IN 100,000.

No.	Aluminum.		Theory.	Phenolsulphonic acid.		
	A.	B.		C.	D.	E.
21 ..	0.0800	0.1080	0.0950	0.1020	0.1000	. . . . .
22 ..	1.2800	1.3000	1.3500	. . . . .	1.2000	1.3000[1]
23 ..	0.0200	0.0140	0.0160	0.0200	0.0150	0.0180
24 ..	0.8000	0.9500	0.8500	0.8530	0.9500	0.9000
25 ..	2.0500	2.5000	2.2100	2.4500	2.5000	2.5000[2]
26 ..	0.0400	0.0340	0.0380	0.0380	. . . . .	0.0400
27 ..	0.0800	0.0660	0.0950	0.1000	0.1000	0.0930
28 ..	0.4200	0.3660	0.4250	0.4150	0.4500	0.4000
29 ..	0.4100	0.4040	0.4250	0.4500	0.4250	0.4000
30 ..	0.0300	0.0460	0.0350	0.0370	0.0270	0.0300
31 ..	0.0130	0.0120	0.0140	0.0215	0.0120	0.0150
32 ..	0.0130	0.0180	0.0140	0.0270	0.0150	0.0150
33 ..	0.0580	0.0640	0.0650	0.0620	0.0600	0.0550
34 ..	0.0610	0.0540	0.0650	0.0740	0.0520	0.0550
35 ..	0.0830	0.0880	0.0900	0.0900	0.0920	0.0700

[1] A later determination gave 1.3250.

[2] A later determination gave 2.1300.

	Aluminum.			Phenolsulphonic.	
No.	Average.	Difference.	Theory.	Average.	Difference.
21 · · · · · · · ·	0.0940	— 0.0010	0.0950	0.1010	+ 0.0060
22 × · · · · ·	1.2900	— 0.0600	1.3500	1.2500	— 0.1000
23 · · · · · · · ·	0.0170	+ 0.0010	0.0160	0.0176	+ 0.0016
24 × · · · · ·	0.8750	+ 0.0250	0.8500	0.9010	+ 0.0510
25 × · · · · ·	2.2750	+ 0.0650	2.2100	2.4833	+ 0.2733
26 · · · · · · · ·	0.0370	— 0.0010	0.0380	0.0390	+ 0.0010
27 · · · · · · · ·	0.0730	— 0.0220	0.0950	0.0976	+ 0.0026
28 · · · · · · · ·	0.3930	— 0.0320	0.4250	0.4216	— 0.0034
29 · · · · · · · ·	0.4070	— 0.0180	0.4250	0.4250	0.0000
30 · · · · · · · ·	0.0380	+ 0.0030	0.0350	0.0313	— 0.0037
31 · · · · · · · ·	0.0125	— 0.0015	0.0140	0.0162	+ 0.0022
32 · · · · · · · ·	0.0155	+ 0.0015	0.0140	0.0190	+ 0.0050
33 · · · · · · · ·	0.0610	— 0.0040	0.0650	0.0590	— 0.0060
34 · · · · · · · ·	0.0575	— 0.0075	0.0650	0.0603	— 0.0047
35 · · · · · · · ·	0.0855	— 0.0045	0.0900	0.0840	— 0.0060
		— 0.0915			— 0.0238
		+ 0.0055			+ 0.0184

Numbers 22, 24, and 25 are very obviously incorrectly estimated by both methods; the aluminum process gave in two of these cases results too high; the phenolsulphonic acid process gave likewise in two cases results too high, probably from errors in reading caused by attempting to estimate too deep colors' (over 0.1300 parts nitrogen in 100,000).

Considering the other twelve determinations, the aluminum process gave results too low in nine, with a total of 0.0915 parts of nitrogen or *6.6 per cent. too low*, and too high in three with a total of 0.0055 parts of nitrogen or *0.4 per cent. too high*. The phenolsulphonic acid process gave too low results in five cases with a total of 0.0238 parts of nitrogen or *1.6 per cent. too low*, and too high in six cases with a total of 0.0184 parts of nitrogen or *1.3 per cent. too high*.

From this investigation it is evident that the aluminum method, in addition to being more troublesome to execute, yields results even in the presence of chlorine (two parts in 100,000) decidedly lower than the phenolsulphonic acid method: further than this, it was observed that duplicate determinations made by the former process did not present a satisfactory agreement.

[1] This the usual result.

This conclusion I am aware is in direct variance with the statement of Hazen and Clark,[1] who say, "This process (phenolsulphonic acid) with proper precautions, gives results usually too low and often much too low."

In addition to the aluminum process, other methods of reduction have been studied: Fricke[2] states that Förster's—the reduction with metallic iron and caustic potash in presence of alcohol—Schmitt's—the reduction with iron and acetic acid—and Ulsch's,—the reduction by 'ferrum reductum' and sulphuric acid—all yield good results, provided 0.5 gram potassium nitrate be present, these are suitable for the valuation of saltpeters and are obviously not sufficiently refined for the purposes of water analysis. The other method of Ulsch[3] by reduction with iron and sulphuric acid and subsequent measurement of the "deficit of hydrogen" is open to the same objection. One milligram potassium nitrate is equivalent to 1.1 cc. of hydrogen, this corresponds to 1.38 parts nitrogen per 100,000.

Harrow's[4] method. the reduction to nitrate in presence of α naphthylamine and sulphanilic acid is sensitive to 0.04 parts nitrogen per 100,000, or twenty times less delicate than the phenolsulphonic acid process. In my opinion advancement in the estimation of nitric acid for the purposes of water analysis is to be sought, not in any method of reduction to ammonia or nitrous acid, but rather in the formation of organic nitro bodies of high coloring power and constant composition, and with this the writer is already engaged.

In conclusion, I desire to express my indebtedness to Mrs. Richards, Miss Hyams, and Mr. Tuttle, of the Massachusetts Board of Health staff for assistance in making many of the above determinations.

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[1] J. Anal. Appl. Chem., 5, 3.

[2] Ztschr. für angew. Chemie. April. 1891. Analyst 16. 117

[3] Ztschr. anal. Chem., 20. 175. Analyst 16, 134.

[4] J. Chem. Soc.. 1891. Trans., 320.