TABLE 4500-NH₃:II.* VALUES OF Q VS. ΔE (59 mV SLOPE) FOR 10% VOLUME CHANGE

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
5.0	0.297	7.0	0.225	9.0	0.178	12.0	0.133	16.0	0.0952	20.0	0.0716	24.0	0.0556	28.0	0.0440	32.0	0.0354	40.0	0.0237
5.1	0.293	7.1	0.222	9.1	0.176	12.2	0.130	16.2	0.0938	20.2	0.0707	24.2	0.0549	28.2	0.0435	32.2	0.0351	41.0	0.0226
5.2	0.288	7.2	0.219	9.2	0.174	12.4	0.128	16.4	0.0924	20.4	0.0698	24.4	0.0543	28.4	0.0431	32.4	0.0347	42.0	0.0216
5.3	0.284	7.3	0.217	9.3	0.173	12.6	0.126	16.6	0.0910	20.6	0.0689	24.6	0.0536	28.6	0.0426	32.6	0.0343	43.0	0.0206
5.4	0.280	7.4	0.214	9.4	0.171	12.8	0.123	16.8	0.0897	20.8	0.0680	24.8	0.0530	28.8	0.0421	32.8	0.0340	44.0	0.0196
5.5	0.276	7.5	0.212	9.5	0.169	13.0	0.121	17.0	0.0884	21.0	0.0671	25.0	0.0523	29.0	0.0417	33.0	0.0335	45.0	0.0187
5.6	0.272	7.6	0.209	9.6	0.167	13.2	0.119	17.2	0.0871	21.2	0.0662	25.2	0.0517	29.2	0.0412	33.2	0.0333	46.0	0.0179
5.7	0.268	7.7	0.207	9.7	0.165	13.4	0.117	17.4	0.0858	21.4	0.0654	25.4	0.0511	29.4	0.0408	33.4	0.0329	47.0	0.0171
5.8	0.264	7.8	0.204	9.8	0.164	13.6	0.115	17.6	0.0846	21.6	0.0645	25.6	0.0505	29.6	0.0403	33.6	0.0326	48.0	0.0163
5.9	0.260	7.9	0.202	9.9	0.162	13.8	0.113	17.8	0.0834	21.8	0.0637	25.8	0.0499	29.8	0.0399	33.8	0.0323	49.0	0.0156
6.0	0.257	8.0	0.199	10.0	0.160	14.0	0.112	18.0	0.0822	22.0	0.0629	26.0	0.0494	30.0	0.0394	34.0	0.0319	50.0	0.0149
6.1	0.253	8.1	0.197	10.2	0.157	14.2	0.110	18.2	0.0811	22.2	0.0621	26.2	0.0488	30.2	0.0390	34.2	0.0316	51.0	0.0143
6.2	0.250	8.2	0.195	10.4	0.154	14.4	0.108	18.4	0.0799	22.4	0.0613	26.4	0.0482	30.4	0.0386	34.4	0.0313	52.0	0.0137
6.3	0.247	8.3	0.193	10.6	0.151	14.6	0.106	18.6	0.0788	22.6	0.0606	26.6	0.0477	30.6	0.0382	34.6	0.0310	53.0	0.0131
6.4	0.243	8.4	0.190	10.8	0.148	14.8	0.105	18.8	0.0777	22.8	0.0598	26.8	0.0471	30.8	0.0378	34.8	0.0307	54.0	0.0125
6.5	0.240	8.5	0.188	11.0	0.145	15.0	0.103	19.0	0.0767	23.0	0.0591	27.0	0.0466	31.0	0.0374	35.0	0.0304	55.0	0.0120
6.6	0.237	8.6	0.186	11.2	0.143	15.2	0.1013	19.2	0.0756	23.2	0.0584	27.2	0.0461	31.2	0.0370	36.0	0.0289	56.0	0.0115
6.7	0.234	8.7	0.184	11.4	0.140	15.4	0.0997	19.4	0.0746	23.4	0.0576	27.4	0.0456	31.4	0.0366	37.0	0.0275	57.0	0.0110
6.8	0.231	8.8	0.182	11.6	0.137	15.6	0.0982	19.6	0.0736	23.6	0.0569	27.6	0.0450	31.6	0.0362	38.0	0.0261	58.0	0.0105
6.9	0.228	8.9	0.180	11.8	0.135	15.8	0.0967	19.8	0.0726	23.8	0.0563	27.8	0.0445	31.8	0.0358	39.0	0.0249	59.0	0.0101

* Orion Research Inc. Instruction Manual, Ammonia Electrode, Model 95-12, Boston, MA. 02129.

trode method yielded a mean recovery of 102% of the values obtained by the phenate method when the NH₃-N concentrations varied between 0.30 and 0.78 mg/L. In 57 wastewater samples similarly compared, the electrode method yielded a mean recovery of 108% of the values obtained by the phenate method using distillation when the NH₃-N concentrations varied between 10.2 and 34.7 mg N/L. In 20 instances in which two to four replicates of these samples were analyzed, the mean standard deviation was 1.32 mg N/L. In three measurements at a sewer outfall, distillation did not change statistically the value obtained by the electrode method. In 12 studies using standards in the 2.5- to 30-mg N/L range, average recovery by the phenate method was 97% and by the electrode method 101%.

4500-NH₃ F.   Phenate Method

1.   General Discussion

a. Principle: An intensely blue compound, indophenol, is formed by the reaction of ammonia, hypochlorite, and phenol catalyzed by sodium nitroprusside.

b. Interferences: Complexing magnesium and calcium with citrate eliminates interference produced by precipitation of these ions at high pH. There is no interference from other trivalent forms of nitrogen. Remove interfering turbidity by distillation or filtration. If hydrogen sulfide is present, remove by acidifying samples to pH 3 with dilute HCl and aerating vigorously until sulfide odor no longer can be detected.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2.   Apparatus

Spectrophotometer for use at 640 nm with a light path of 1 cm or greater.

3.   Reagents

a. Phenol solution: Mix 11.1 mL liquified phenol (≥89%) with 95% v/v ethyl alcohol to a final volume of 100 mL. Prepare weekly. **CAUTION: Wear gloves and eye protection when handling phenol; use good ventilation to minimize all personnel exposure to this toxic volatile substance.**

b. Sodium nitroprusside, 0.5% w/v: Dissolve 0.5 g sodium nitroprusside in 100 mL deionized water. Store in amber bottle for up to 1 month.

c. Alkaline citrate: Dissolve 200 g trisodium citrate and 10 g sodium hydroxide in deionized water. Dilute to 1000 mL.

d. Sodium hypochlorite, commercial solution, about 5%. This solution slowly decomposes once the seal on the bottle cap is broken. Replace about every 2 months.

e. Oxidizing solution: Mix 100 mL alkaline citrate solution with 25 mL sodium hypochlorite. Prepare fresh daily.

f. Stock ammonium solution: See 4500-NH₃.D.3d.

g. Standard ammonium solution: Use stock ammonium solution and water to prepare a calibration curve in a range appropriate for the concentrations of the samples.

4. Procedure

To a 25-mL sample in a 50-mL Erlenmeyer flask, add, with thorough mixing after each addition, 1 mL phenol solution, 1 mL sodium nitroprusside solution, and 2.5 mL oxidizing solution. Cover samples with plastic wrap or paraffin wrapper film. Let color develop at room temperature (22 to 27°C) in subdued light for at least 1 h. Color is stable for 24 h. Measure absorbance at 640 nm. Prepare a blank and at least two other standards by diluting stock ammonia solution into the sample concentration range. Treat standards the same as samples.

5. Calculations

Prepare a standard curve by plotting absorbance readings of standards against ammonia concentrations of standards. Compute sample concentration by comparing sample absorbance with the standard curve.

6. Precision and Bias

For the manual phenate method, reagent water solutions of ammonium sulfate were prepared and analyzed by two analysts in each of three laboratories. Results are summarized in Table 4500-NH$_3$:III.

TABLE 4500-NH$_3$:III. PRECISION DATA FOR MANUAL PHENATE METHOD BASED ON TRIPLICATE ANALYSES OF AMMONIUM SULFATE

Lab/ Analyst	NH$_3$-N Concentration *mg/L*	Optical Density	Relative Standard Deviation %
1/1	0.1	0.129	1.55
1/2	0.1	0.114	9.66
2/1	0.1	0.100	10.2
2/2	0.1	0.122	2.36
3/1	0.1	0.112	3.61
3/2	0.1	0.107	1.94
1/1	0.3	0.393	0.39
1/2	0.3	0.364	0.32
2/1	0.3	0.372	2.64
2/2	0.3	0.339	0.90
3/1	0.3	0.370	0.31
3/2	0.3	0.373	0.46
1/1	0.5	0.637	0.77
1/2	0.5	0.630	0.56
2/1	0.5	0.624	1.65
2/2	0.5	0.618	0.86
3/1	0.5	0.561	0.27
3/2	0.5	0.569	0.91

7. Bibliography

SOLORZANO, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. *Limnol. Oceanogr.* 14:799.

PARSONS, T.R., Y. MAITA & C.M. LALLI. 1984. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, Elmsford, N.Y.

4500-NH$_3$ G.   Automated Phenate Method

1. General Discussion

a. Principle: Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.

b. Interferences: Seawater contains calcium and magnesium ions in sufficient concentrations to cause precipitation during analysis. Adding EDTA and sodium potassium tartrate reduces the problem. Eliminate any marked variation in acidity or alkalinity among samples because intensity of measured color is pH-dependent. Likewise, ensure that pH of wash water and standard ammonia solutions approximates that of sample. For example, if sample has been preserved with 0.8 mL conc H$_2$SO$_4$/L, include 0.8 mL conc H$_2$SO$_4$/L in wash water and standards. Remove interfering turbidity by filtration. Color in the samples that absorbs in the photometric range used for analysis interferes.

c. Application: Ammonia nitrogen can be determined in potable, surface, and saline waters as well as domestic and industrial wastewaters over a range of 0.02 to 2.0 mg/L when photometric measurement is made at 630 to 660 nm in a 10- to 50-mm tubular flow cell at rates of up to 60 samples/h. Determine higher concentrations by diluting the sample.

d. Quality control (QC): The QC practices considered to an integral part of each method are summarized in Table 4020:I.

2. Apparatus

Automated analytical equipment: An example of the required continuous-flow analytical instrument consists of the interchangeable components shown in Figure 4500-NH$_3$:1.

3. Reagents

a. Ammonia-free distilled water: See 4500-NH$_3$.B.3*a*2. Use for preparing all reagents and dilutions.

b. Sulfuric acid (H$_2$SO$_4$), 5*N*, air scrubber solution: Carefully add 139 mL conc H$_2$SO$_4$ to approximately 500 mL water, cool to room temperature, and dilute to 1 L.