FINAL

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION
CHEMISTRY LABORATORY METHODS MANUAL, TALLAHASSEE

CALCULATION OF UN-IONIZED AMMONIA IN FRESH WATER
STORET Parameter Code 00619

Background

The calculation technique presented here is for estimating the concentration of un-ionized ammonia in fresh water based on the data and information provided by Thurston, et. al. (Reference 1). Although the method was developed for solutions of zero salinity, it is applicable to dilute saline solutions without serious error **(see note, below)**.

Summary of Method

In aqueous solution, unionized ammonia exists in equilibrium with ammonium ion and hydroxide ion. The equilibrium constant for this reaction is a function of temperature and solution pH. Thus, if the equilibrium constant is known for a particular temperature and the pH of the solution is also known, the fraction of un-ionized ammonia can be calculated. Then, if the total ammonium concentration is known from laboratory analysis, the un-ionized ammonia concentration can be calculated.

It must be noted however that the concentration of un-ionized ammonia is also dependent on the ionic strength of the solution. There is a slight decrease in the un-ionized ammonia fraction of total ammonia as the ionic strength of the solution increases. A method to estimate un-ionized ammonia in saline waters is provided in Appendix III.

WARNING: Before using these procedures to determine Un-ionized Ammonia, one must study the equations in the following sections to obtain an understanding of the influence of the several measured parameters - Total Ammonium, mg/L; Temperature, ^{O}C; pH, units; and Salinity, ppt (if salinity corrections are appropriate) - on the resultant Un-ionized Ammonia value. While a detailed analysis will not be presented here, the errors which may be tolerated for these parameters in order to report Un-ionized Ammonia to two significant figures are given in the table below:

Note: For saline (marine or brackish) water with salinity (in parts per thousand, o/oo) of 5 o/oo to 35 o/oo and temperature from 5^{O}C to 35^{O}C and pH from 7.8 to 8.3; see Appendix III.

CAUTION: Un-ionized Ammonia data obtained using the salinity correction calculations of Appendix III are not approved for STORET entry under STORET Code 00619.

Parameter	Error

Total Ammonia (mg/L)	+/- 5%
Field Temperature (°C)	+/- 0.1 °C
Field pH (units)	+/- 0.1 unit
Salinity (ppt)	+/- 1 ppt

NOTE: these are total measurement errors including precision and accuracy. Except for field pH, the usual measurement methods for these parameters commonly yield equal or smaller uncertainties than those stated above. Extreme care should be exercised in the measurement of pH to be within +/- 0.1 unit of the true value. Salinity may be measured in the field or in the laboratory, following the prescribed methods and sample handling in the DEP regulations (see Chapter 62-160 FAC).

Definition of Terms Used in Calculations

1. Overall chemical equilibrium involved:

$$NH_3\,(g) + nHOH \overset{K_1}{=} NH_3{\cdot}nHOH\,(aq.) \overset{K_2}{=} NH_4^+ + OH^- + (n-1)HOH\,(l)$$

The equilibrium associated with K_1, can be considered to be negligible in its effect on subsequent calculations only if the sample is collected correctly and if field temperature and field pH measurements are made promptly. **Temperature and pH values other than field measurements cannot be used.**

2. Chemical equilibrium used in calculations:

$$NH_3{\cdot}nHOH\,(aq.) \overset{K_2}{=} NH_4^+ + OH^- + (n-1)HOH$$

Although the dissolved ammonia molecule exists in hydrated form and is associated with at least three water molecules (Reference 2), the equation can be simplified:

$$NH_3{\cdot}HOH \overset{K_2}{=} NH_4^+ + OH^-$$

and the equilibrium constant $K_2 = [NH_4^+][OH^-]/[NH_3{\cdot}HOH]$ where

$K_2 = K_b$ = equilibrium constant (base form)

$[NH_4^+]$ = concentration of ammonium ion, mole/L

$[NH_3{\cdot}HOH]$ = concentration of un-ionized ammonia, mole/L

$[OH^-]$ = concentration of hydroxide ion, mole/L

$[H^+]$= concentration of hydronium ion, mole/L

3. Other Terms Used:

$K_w = [H^+][OH^-]$ equilibrium constant for water

$K_w = K_a K_b$ acid/base/water equilibrium constant relation

$pH = -\log [H^+]$ definition

$pK_a = -\log K_a$ definition

$pK_b = -\log K_b$ definition

4. Equilibrium Constant - Temperature Relation

The key to this entire calculation technique was the establishment of a satisfactory empirical mathematical expression relating the equilibrium constant and the temperature. Within the temperature range of 0^oC-50^oC and a pH range of 6.0 to 10.0, this expression is:

$$pK_a = 0.0901821 + 2729.92/T_k$$

where T_k is temperature in degrees Kelvin, $T_k = {}^oC + 273.2$.

5. Un-ionized Ammonia

The fraction of un-ionized ammonia is given by the following expression (see Appendix I):

$$f = 1/(10^{(pKa-pH)} + 1)$$

6. Calculations

$$f = [NH_3 \cdot HOH]/([NH_4^+] + [NH_3 \cdot HOH])$$

= (un-ionized ammonia, mole/L)/(total ammonia, mole/L)

where f is actually the mole fraction of un-ionized ammonia.

Concentration units other than mole/L can be used to describe both un-ionized ammonia and total ammonia. However, the units must be identical for each in these calculations for the constant f to remain numerically correct.

The usual laboratory results for ammonia analysis are for total ammonia-nitrogen and are expressed in terms of total ammonia-nitrogen,

$(NH_3 - N)_t$, mg/L

where:

$$(NH_3 - N)_t = (NH_3 \cdot HOH - N) + (NH_4^+ - N)$$

(total ammonia - nitrogen, mg/l)$_t$ =(unionized ammonia - nitrogen, mg/l) + (ammonium ion-nitrogen,mg/l).

The fraction of un-ionized ammonia can be expressed as:

$$f = ((NH_3 \cdot HOH - N), mg/L)/((NH_3 - N)_t, mg/L)$$

Note that the concentration units for both numerator and denominator are identical.

Thus, if the fraction of un-ionized ammonia is known for a particular temperature and pH and the laboratory analytical results for total ammonia-nitrogen, mg/L, is known, the un-ionized ammonia-nitrogen, mg/L, can be calculated.

However, it is desired that concentration of un-ionized ammonia be expressed in terms of mg/L ammonia, not mg/L ammonia-nitrogen. A conversion will be necessary using the appropriate formula weights:

$$(NH_3 \cdot HOH - N) \text{ mg/L} \times (17/14) = (NH_3) \text{ mg/L}.$$

(un-ionized ammonia, as mg/L nitrogen)(17/14) = (un-ionized ammonia as mg/L NH_3).

7. Example

The following field and laboratory data were obtained for a fresh water sample collected in the vicinity of Palatka.

Field temperature, T = 18.5^{o}C

Field pH, pH = 8.3

Total ammonia-nitrogen, $(NH_3 - N)_t$ = 2.20 mg/L

From APPENDIX II (Reference 1), the percent un-ionized ammonia at pH = 8.3 and T = 18.5^{o}C is 6.63%. Therefore, the fraction of un-ionized ammonia is f = 0.0663. The concentration of un-ionized ammonia is:

$$(NH_3 - N)_t (.0663) = (NH_3 - N)_{un\text{-}ionized}, \text{ mg/L}$$

(2.20) (.0663) = (.146) mg/L - nitrogen

This is then converted to mg/L un-ionized ammonia:

(0.146) (17/14) = 0.177 mg/L un-ionized ammonia, as NH_3.

If the uncertainties in the input parameters are equal or better than those given on page 2 (top table), the final result can be reported to at least two significant figures. Therefore, for this example, the reported result for the concentration of un-ionized ammonia would be 0.18 mg/L (STORET 00619).

NOTES

(a) The tabulation provided in this SOP (Appendix II) should suffice for most calculations of Un-ionized Ammonia. Tables with finer grid (i.e. Temperature and pH in smaller incremental values) are found in Reference 3.

(b) This reprinted version of the 1983 procedure has been edited and finalized by the staff of the DEP EA Section. Only minor editorial corrections have been made to the original version which was prepared by R.H. Patton, Jack Merritt, and Thomas L. Stevens, DEP-Chemistry.

(c) A spreadsheet calculation in MS Excel is available to obtain values of un-ionized ammonia by entering the measured parameters (total ammonia-N, temperature, pH, and salinity). The excel file is posted for download with this SOP on the DEP website. The spreadsheet uses equations A and B from appendix III, along with the definition of the fraction ratio corrected by the molecular weights. The spreadsheet is useful for both fresh and saline waters and was prepared by Landon Ross, DEP-Biology.

References

1. Thurston, et. al., (1974). Aqueous Ammonia Equilibrium Calculations. Technical Report No. 74-1, Fisheries Bioassay Laboratory, Montana State University, Bozeman, MT., July 1977 Revision.

2. Butler, J. N. 1964. Ionic Equilibrium. Addison-Wesley Publishing Company, Inc., Reading, HA. p. 129.

3. Thurston, et. al., (1979). Aqueous Ammonia Equilibrium-Tabulation of Percent Un-ionized Ammonia. EPA-600/3-79-091, Environmental Research Laboratory, Duluth, MN 55804. Available from NTIS (PB80-103518).

Appendix I.

K_b

$NH_3{\cdot}HOH = NH_4^+ + OH^-$

$K_b = [NH_4^+][OH^-]/[NH_3{\cdot}HOH]$ (1)

Reminder: $K_w = [H^+] (OH^-]$ (2)

Reminder: $K_w = K_aK_b$ (3)

Use (3) and (2) to convert (1) to:

$K_w/K_a = ([NH_4^+]/[NH_3{\cdot}HOH])(K_w/[H^+])$

Simplify and rearrange to:

$K_a = [H^+][NH_3{\cdot}HOH]/[NH_4^+]$ (4)

Take log of both sides and multiply by -1.

$-\log K_a = -\log [H^+] - \log [NH_3{\cdot}HOH]/[NH_4^+]$

Reminder: $-\log K_a = pK_a$

Reminder: $-\log [H^+] = pH$

Substitute, invert other log argument, and change sign:

$pK_a = pH + \log [NH_4^+]/[NH_3.HOH]$

Rearrange and raise each side to exponent of 10:

$10^{(pKa - pH)} = 10^{\log [NH4+]/[NH3.HOH]}$

Simplify:

$10^{(pKa - pH)} = [NH_4^+]/[NH_3{\cdot}HOH]$

Add 1 to both sides and simplify:

$10^{(pKa - pH)} + 1 = ([NH_4^+] + [NH_3{\cdot}HOH])/[NH_3{\cdot}HOH]$

Take the reciprocal of each side:

$1/(10^{(pKa - pH)} + 1) = [NH_3{\cdot}HOH]/([NH_4^+] + [NH_3{\cdot}HOH])$ (5)

Reminder: $[NH_3{\cdot}HOH]$ = concentration of un-ionized ammonia, mole/L

Reminder: $[NH_4] + [NH_3 \cdot HOH]$ = concentration of
total ammonia, mole/L

Appendix I. (continued)

The right-hand side of (5) is equal to f, the fraction (mole fraction) of un-ionized ammonia. (See page 7 of Reference 1.) Also, f x 100 is the un-ionized ammonia percent (the numerical values in Table 2 of Reference 1).

Therefore, (5) can be expressed as:

$$1/(10^{(pKa - pH)} + 1) = f, \text{ mole fraction un-ionized ammonia} \qquad (6)$$

Reminder: Laboratory results for total ammonia are usually reported in terms of ammonia-nitrogen, mg/L; not mole/L. DEP rules (Chapter 62-302 FAC) describe the water quality standard for un-ionized ammonia in terms of mg/L. Laboratory results should be reported in the same terms.

APPENDIX II.

Table 2

Percent Un-ionized NH_3, in Aqueous Ammonia Solutions
For 15^{o}C-30^{o}C and pH 6-1O

Temperature, ^{o}C

pH	15.5	16.0	16.5	17.0	17.5	18.0	18.5	19.0	19.5
6.0	.0284	.0295	.0306	.0318	.032O	.0343	.0356	.0369	.0383
6.1	.0358	.0372	.0386	.0401	.0416	.043l	.0448	.0465	.0482
6.2	.0451	.0468	.0486	.0504	.0523	.0543	.0564	.0585	.0607
6.3	.0567	.0589	.0611	.0635	.0659	.0684	.0709	.0736	.0763
6.4	.0714	.0741	.0759	.0799	.0829	.0860	.0893	.0925	.0961
6.5	.0898	.0933	.0968	.101	.104	.108	.112	.1l7	.121
6.6	.113	.117	.122	.127	.131	.126	.141	.147	.152
6.7	.142	.148	.153	.159	.165	.172	.178	.185	.192
6.8	.179	.186	.193	.200	.208	.216	.224	.232	.241
6.9	.225	.234	.243	.252	.262	.272	.282	.292	.303
7.0	.284	.294	.306	.317	.329	.342	.355	.368	.381
7.1	.357	.370	.384	.399	.414	.430	.446	.463	.480
7.2	.449	.466	.483	.502	.521	.540	.561	.582	.603
7.3	.564	.586	.608	.631	.655	.679	.705	.731	.758
7.4	.709	.736	.764	.793	.823	.854	.886	.919	.953
7.5	.891	.925	.960	.996	1.03	1.07	1.11	1.15	1.20
7.6	1.12	1.16	1.21	1.25	1.30	1.35	1.40	1.45	1.50
7.7	1.41	1.46	1.51	1.57	1.63	1.69	1.75	1.82	1.88
7.8	1.76	1.83	1.90	1.97	2.04	2.12	2.20	2.28	2.36
7.9	2.21	2.29	2.38	2.47	2.56	2.65	2.75	2.85	2.95
8.0	2.77	2.87	2.97	3.08	3.20	3.31	3.44	3.56	3.69
8.1	3.46	3.58	3.72	3.85	3.99	4.14	4.29	4.44	4.60
8.2	4.31	4.47	4.63	4.80	4.98	5.15	5.34	5.53	5.72
8.3	5.37	5.56	5.76	5.97	6.18	6.40	6.63	6.86	7.10
8.4	5.67	5.91	7.15	7.40	7.66	7.93	8.20	8.49	8.77
8.5	8.25	8.54	8.84	9.14	9.46	9.78	10.1	10.5	10.8
8.6	l0.2	10.5	10.9	11.2	11.6	12.0	12.4	12.8	13.2
8.7	12.5	12.9	13.3	13.8	14.2	14.7	15.1	15.6	16.1
8.8	15.2	15.7	16.2	16.7	17.2	17.8	18.3	18.9	19.5
8.9	18.4	19.0	19.6	2O.2	20.8	21.4	22.0	22.7	23.3
9.0	22.1	22.8	23.5	24.1	24.8	25.5	26.2	27.0	27.7
9.1	26.4	27.1	27.8	28.6	29.4	30.1	30.9	31.7	32.5
9.2	31.1	31.9	32.7	33.5	34.4	35.2	36.1	36.9	37.3
9.3	36.2	37.1	38.0	38.8	39.7	40.6	41.5	42.4	43.3
9.4	41.7	42.6	43.5	44.4	45.4	46.3	47.2	48.1	49.0
9.5	47.3	48.3	49.2	50.2	51.1	52.0	52.9	53.9	54.8
9.6	53.1	54.0	55.0	55.9	56.8	57.7	58.6	59.5	60.4
9.7	58.8	59.7	60.6	61.5	62.3	63.2	64.1	64.9	65.7

9.8	64.2	65.1	65.9	66.8	67.6	68.4	69.2	70.0	70.7
9.9	69.3	70.1	70.9	71.7	72.4	73.1	73.9	74.5	75.3
10.0	74.0	74.7	75.4	76.1	76.8	77.4	78.1	78.7	79.3

<u>APPENDIX II.</u> (continued)

(Table 2, continued)

Percent Un-ionized NH_3, in Aqueous Ammonia Solutions

Temperature, ^{o}C

pH	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.3	24.5	25.0
6.0	.0397	.0412	.0427	.0443	.0459	.0476	.0493	.05ll	.0530	.0549	.0569
6.1	.0500	.0518	.0538	.0557	.0578	.0599	.0621	.0644	.0667	.0691	.0716
6.2	.0629	.0653	.0677	.0702	.0727	.0754	.0782	.0810	.0839	.0870	.0901
6.3	.0792	.0821	.0852	.0883	.0916	.0949	.0984	.102	.106	.109	.113
6.4	.0997	.103	.107	.111	.115	.119	.124	.128	.133	.138	.143
6.5	.125	.130	.135	.140	.145	.150	.156	.162	.167	.173	.180
6.6	.158	.164	.170	.176	.183	.189	.196	.203	.211	.218	.225
6.7	.199	.206	.214	.222	.230	.238	.247	.256	.265	.275	.284
6.8	.250	.259	.269	.279	.289	.300	.310	.322	.333	.345	.358
6.9	.315	.326	.338	.35l	.364	.377	.390	.405	.419	.434	.450
7.0	.396	.410	.425	.44l	.457	.474	.491	.509	.527	.546	.566
7.1	.498	.516	.535	.555	.575	.596	.617	.640	.663	.687	.711
7.2	.625	.649	.673	.697	.723	.749	.776	.804	.833	.863	.894
7.3	.786	.815	.845	.876	.908	.941	.975	1.01	1.05	1.08	1.12
7.4	.988	1.02	1.06	1.10	1.14	1.18	1.22	1.27	1.31	1.36	1.41
7.5	1.24	1.29	1.33	1.38	1.43	1.48	1.54	1.59	1.65	1.71	1.77
7.6	1.56	1.61	1.67	1.73	1.80	1.86	1.93	2.00	2.07	2.14	2.22
7.7	1.95	2.02	2.10	2.17	2.25	2.33	2.41	2.5O	2.59	2.68	2.77
7.8	2.44	2.53	2.63	2.72	2.82	2.92	3.02	3.13	3.24	3.35	3.47
7.9	3.06	3.17	3.28	3.40	3.52	3.64	3.77	3.90	4.04	4.18	4.33
8.0	3.82	3.96	4.10	4.24	4.39	4.55	4.70	4.87	5.03	5.21	5.38
8.1	4.76	4.93	5.10	5.28	5.47	5.66	5.85	6.05	6.25	6.47	6.69
8.2	5.92	6.13	6.34	6.56	6.79	7.02	7.25	7.50	7.75	8.01	8.27
8.3	7.34	7.60	7.86	8.12	8.39	8.68	8.96	9.25	9.56	9.88	l0.2
8.4	9.07	9.38	9.69	10.0	10.3	10.7	11.0	11.4	11.7	12.1	12.5
8.5	11.2	11.5	11.9	12.3	12.7	13.1	13.5	13.9	14.4	14.8	15.3
8.6	13.7	14.1	14.5	15.0	15.5	15.9	16.4	16.9	17.4	17.9	18.5
8.7	16.6	17.1	17.6	18.2	18.7	19.3	19.8	20.4	21.0	21.5	22.2
8.8	20.0	20.6	21.2	21.8	22.5	23.1	23.7	24.4	25.l	25.7	26.4
8.9	24.0	24.7	25.3	26.0	26.7	27.4	28.2	28.9	29.6	30.4	31.1
9.0	28.4	29.2	29.9	30.7	31.5	32.3	33.0	33.8	34.5	35.5	36.3
9.1	33.3	34.2	35.0	35.8	36.6	37.5	38.3	39.2	40.0	40.9	41.7

9.Z	38.6	39.5	40.4	41.2	42.1	43.0	43.9	44.8	45.7	46.5	47.4
9.3	44.2	45.1	46.0	46.9	47.8	48.7	49.6	50.5	51.4	52.3	53.2
9.4	49.9	50.9	51.8	52.7	53.6	54.5	55.4	56.2	57.1	58.0	58.8
9.5	55.7	56.6	57.5	58.3	59.2	60.1	60.9	61.8	62.5	63.5	64.3
9.6	61.3	62.1	63.0	63.8	64.6	65.5	66.3	67.1	67.8	68.5	69.4
9.7	66.6	67.4	68.2	68.9	69.7	70.5	71.2	71.9	72.7	73.4	74.0
9.8	71.6	72.2	72.9	73.7	74.3	75.O	75.7	76.3	77.0	77.6	78.2
9.9	75.9	76.6	77.2	77.9	78.4	79.1	79.7	80.3	80.8	81.4	81.9
10.0	79.9	80.5	81.0	81.5	82.1	82.6	83.2	83.5	84.1	84.5	85.1

APPENDIX II. (continued)

(Table 2, continued)

Percent Un-ionized NH3 in Aqueous Ammonia Solutions

Temperature, ^{O}C

pH	25.5	26.0	26.5	27.0	27.5	28.0	23.5	29.0	29.5	30.0
6.0	.0589	.0610	.0632	.0654	.0678	.0701	.0726	.0752	.0778	.0805
6.1	.0742	.0768	.0796	.0824	.0853	.0883	.0914	.0946	.0979	.101
6.2	.0933	.0967	.100	.104	.107	.111	.115	.119	.123	.129
6.3	.117	.122	.126	.130	.135	.140	.145	.150	.155	.160
6.4	.148	.153	.159	.164	.170	.176	.182	.189	.195	.202
6.5	.186	.193	.200	.207	.214	.221	.229	.237	.246	.254
6.6	.234	.242	.251	.260	.269	.279	.289	.299	.309	.320
6.7	.295	.305	.316	.327	.339	.351	.363	.376	.389	.402
6.8	.371	.384	.397	.4ll	.426	.441	.456	.472	.489	.506
6.9	.466	.483	.500	.517	.536	.554	.574	.594	.615	.636
7.0	.586	.607	.628	.651	.674	.697	.722	.747	.772	.799
7.1	.737	.763	.790	.818	.846	.876	.907	.938	.970	1.0O
7.2	.926	.958	.992	1.03	1.06	1.10	1.14	1.18	1.22	1.25
7.3	1.16	1.20	1.25	1.29	1.33	1.38	1.43	1.48	l.53	1.58
7.4	1.46	1.51	1.56	1.62	1.67	1.73	1.79	1.85	1.92	1.98
7.5	1.83	1.89	1.96	2.03	2.10	2.17	2.25	2.32	2.40	2.48
7.6	2.29	2.37	2.46	2.54	2.63	2.72	2.81	2.91	3.01	3.11
7.7	2.87	2.97	3.07	3.18	3.29	3.40	3.5l	3.63	2.75	3.88
7.8	3.59	3.71	3.84	3.97	4.10	4.24	4.38	4.53	4.68	4.84
7.9	4.47	4.53	4.78	4.94	5.11	5.28	5.46	5.64	5.82	6.0l
8.0	5.57	5.75	5.95	6.15	6.35	6.56	6.78	7.00	7.22	7.46
8.1	6.91	7.14	7.37	7.62	7.87	8.12	8.38	8.65	8.92	9.2l
8.2	8.54	8.82	9.11	9.40	9.70	10.0	10.3	10.7	11.0	11.3
8.3	10.5	10.9	11.2	11.5	11.9	12.3	12.7	13.0	13.4	13.8
3.4	12.9	13.3	13.7	14.1	14.5	15.0	15.4	15.9	16.4	16.8
8.5	15.7	16.2	16.7	17.2	17.7	18.2	18.7	19.2	19.8	2O.3

8.6	19.0	19.6	20.1	20.7	21.3	21.8	22.4	23.0	23.7	24.3
8.7	22.8	23.4	24.1	24.7	25.4	26.0	26.7	27.4	28.1	28.8
8.8	27.1	27.8	28.5	29.2	30.0	30.7	31.4	32.2	32.9	33.7
8.9	31.9	32.7	33.4	34.2	35.O	35.8	36.6	37.4	38.2	39.0
9.0	37.1	37.9	38.7	39.6	40.4	41.2	42.1	42.9	43.8	44.6
9.1	42.5	43.5	44.3	45.2	46.1	46.9	47.8	48.5	49.5	50.4
9.2	48.3	49.2	50.1	50.9	51.3	52.7	53.5	54.4	55.2	56.1
9.3	54.0	54.9	55.8	56.6	57.5	58.3	59.2	6O.0	60.8	61.6
9.4	59.7	60.5	61.4	62.2	63.0	63.8	64.6	65.4	66.2	66.9
9.5	65.1	65.9	66.7	67.4	68.2	68.9	69.7	70.4	71.1	71.8
9.6	70.1	70.8	71.6	72.3	73.0	73.6	74.3	75.0	75.6	76.2
9.7	74.7	75.4	76.0	76.6	77.3	77.9	78.5	79.0	79.6	80.1
9.8	78.8	79.4	80.0	80.5	81.1	81.6	82.1	82.6	83.1	83.6
9.9	82.4	82.9	83.4	83.9	84.3	84.8	85.2	85.7	86.1	86.5
10.0	85.5	85.9	86.3	86.8	87.1	87.5	87.9	88.3	88.6	89.0

Appendix III.

CALCULATION OF UN-IONIZED AMMONIA IN SALINE WATERS

If data are obtained for a particular sample for salinity in parts per thousand (o/oo), total ammonia (mg/L), temperature (^{o}C) and pH (units), and provided the salinity is in the range - 5 to 35 o/oo, the sample temperature is between 5^{o}C and 35^{o}C, and the pH is in the range 7.8 to 8.3, one may calculate a salinity-corrected value for un-ionized ammonia.

An empirical Equilibrium Constant - Temperature - Salinity Relation was described by Spotte and Adams (Reference A.III.1). However, two equations were incorrect in the article presented by Spotte and Adams; those below (A) and (B) have been corrected to reflect the sources from which these equations were copied - Thurston, Khoo, and Whitfield (see References). From these equations, an f factor, f_s which is the fraction of total ammonia in a sample of saline water which is un-ionized, may be calculated:

$$pK_{a,s} = 0.0901821 + 2729.92/(T + 273.2) + (0.1552 - 0.0003142T)I \quad (A)$$

where

$$I = 19.9273S/(1000 - 1.005109S) \quad (B)$$

and

$pK_{a,s}$ = the ionization constant of ammonium ion in aqueous saline solution (seawater)

T = temperature (^{o}C)

I = molal ionic strength

S = salinity (o/oo)

The $pK_{a,s}$ values can then be used to calculate the f_s values as described on page 2 (Section 4.):

$$f_s = 1/(10^{(pka,s - pH)} + 1)$$

In turn, f_s may be used to calculate the un-ionized ammonia in the saline water sample (Sections 6. & 7.).

For convenience, Tables A.III may be used to estimate un-ionized ammonia. Note, however, that the values in Table A.III are in terms of $1/f_s$, i.e., the reciprocal of the un-ionized ammonia to total ammonium ratio.

Therefore, the calculation example (Section 7) with correction for a salinity of 20 o/oo and where:

Field temperature, T = 18.5^{o}C

Field pH = 8.3

Total ammonia-nitrogen, $(NH_3\text{-}N)_t$ = 2.20 mg/L,

Appendix III. (continued)

The protocol using the Tables A.III is as follows:

From Tables A.III, Table 6. the reciprocal, $1/f_S$ of the un-ionized ammonia-nitrogen to total ammonia nitrogen is 17.3 (See Table 6. by linear interpolation from $1/f_S$ = 17.9 at 18^oC and $1/f_S$ = 16.7 at 19^oC).

Thus,

$1/f_S = 17.3$, then $f_S = 1/17.3 = 0.0578035$

is the fraction of un-ionized amonia-nitrogen to total ammonia-nitrogen.

Thus,

$(NH_3\text{-}N)_t$ (0.0578035) = $(NH_3\text{-}N)_{un\text{-}ionized,}$mg/L

and

2.20(0.0578035) = (0.1272) mg/L - nitrogen.

Then this is converted to mg/L unionized ammonia:

(0.1272) (17/14) = 0.154 mg/L un-ionized ammonia, as NH_3.

If the uncertainties in the input parameters are equal or better than those given on page 2 (top table), the final result can be reported to at least two significant figures. Therefore, the reported result would be:

Concentration of Un-ionized Ammonia = 0.15 mg/L

References

A. III. 1. Spotte, S. and Adams, G., (1983). Estimation of the Allowable Upper Limit of Ammonia in Saline Waters. Marine Ecology - Progress Series, Vol. 10: 207-210.

A. III. 2. Khoo, K. H., Culberson, C. H., and Bates, R. G. (1977).
Thermodynamics of the Dissociation of Ammonia Ion in Seawater from 5 to 40^oC. J. Soln. Chem. 6: 281-290.

A. III. 3. Whitfield, M. (1974). The Hydrolysis of Ammonia Ions in Seawater - a Theoretical Study. J. Mar. Biol. Ass. U. K. 54: 565-580.

TABLES A III.

Table 1. Ratio of total NH_4-N to NH_3-N at pH 7.8 and varying temperature and salinity

pH=7.8 Salinity (o/oo)

T(C^{O})	5	10	15	20	25	30	35
5	133.4	138.2	143.3	148.6	154.1	159.9	166.0
6	123.1	127.5	132.2	137.0	142.2	147.5	153.1
7	113.7	117.7	122.0	126.5	131.2	136.1	14l.3
8	105.0	108.8	112.7	116.8	121.2	125.7	130.5
9	97.1	100.5	104.2	108.0	112.0	116.1	120.5
10	89.8	93.0	96.3	99.9	103.5	107.4	111.4
11	83.1	86.1	89.2	92.4	95.8	99.3	103.1
12	77.0	79.7	82.6	85.5	88.7	92.0	95.4
13	71.3	73.9	76.5	79.2	82.1	85.2	88.3
14	66.1	68.5	70.9	73.5	76.1	78.9	81.9
15	61.4	63.5	65.8	68.1	70.6	73.2	75.9
16	57.0	59.0	61.1	63.2	65.5	67.9	70.4
17	52.9	54.8	56.7	58.7	60.8	63.1	65.4
18	49.2	50.9	52.7	54.6	56.5	58.6	60.7
19	45.8	47.4	49.0	50.7	52.6	54.5	56.4
20	42.6	44.1	45.6	47.2	48.9	50.7	52.5
21	39.7	41.0	42.5	43.9	45.5	47.1	48.9
22	37.0	38.2	39.5	40.9	42.4	43.9	45.5
23	34.5	35.6	36.9	38.1	39.5	40.9	42.4
24	32.2	33.2	34.4	35.6	36.8	38.1	39.5
25	30.0	31.0	32.1	33.2	34.4	35.6	36.8
26	28.0	29.0	30.0	31.0	32.1	33.2	34.4
27	26.2	27.1	28.0	29.0	30.0	31.0	32.1
28	24.5	25.3	26.2	27.1	28.0	29.0	30.0
29	22.9	23.7	24.5	25.3	26.2	27.1	28.1
30	21.5	22.2	22.9	23.7	24.5	25.4	26.2
31	20.1	20.8	21.5	22.2	23.0	23.7	24.6
32	18.9	19.5	20.1	20.8	21.5	22.2	23.0
33	17.7	18.3	18.9	19.5	20.2	20.9	21.6
34	16.6	17.2	17.7	18.3	18.9	19.6	20.2
35	15.6	16.1	16.6	17.2	17.8	l8.4	19.0

Table 2. Ratio of total NH_4-N to NH_3-N at pH 7.9 and varying temperature and salinity

pH=7.9 Salinity (o/oo)

T(C^{O})	5	10	15	20	25	30	35
5	106.2	110.0	114.0	118.2	122.6	127.2	132.1
6	98.0	101.5	105.2	109.1	113.1	117.4	121.8
7	90.5	93.7	97.1	100.7	104.4	108.3	112.4
8	83.6	86.6	89.7	93.0	96.4	100.1	103.8
9	77.3	80.1	83.0	86.0	89.1	92.5	95.9
10	71.5	74.1	76.7	79.5	82.4	85.5	88.7
11	66.2	68.6	71.0	73.6	76.3	79.1	82.1
12	61.3	63.5	65.8	68.2	70.6	73.2	76.0

13	56.9	58.9	61.0	63.2	65.5	67.9	70.4
14	52.7	54.6	56.5	58.6	60.7	62.9	65.2
15	49.0	50.7	52.5	54.3	56.3	58.4	60.5
16	45.5	47.1	48.7	50.4	52.3	54.2	56.2
17	42.3	43.7	45.3	46.9	48.5	50.3	52.1
18	39.3	40.6	42.1	43.6	45.1	46.7	48.4
19	36.6	37.8	39.1	40.5	42.0	43.5	45.0
20	34.0	35.2	36.4	37.7	39.0	40.4	41.9
21	31.7	32.8	33.9	35.1	36.4	37.6	39.0
22	29.6	30.6	31.6	32.7	33.9	35.1	36.3
23	27.6	28.5	29.5	30.5	31.6	32.7	33.9
24	25.7	26.6	27.5	28.5	29.5	30.5	31.6
25	24.0	24.9	25.7	26.6	27.5	28.5	29.5
26	22.5	23.2	24.0	24.8	25.7	26.6	27.5
27	21.0	21.7	22.4	23.2	24.0	24.8	25.7
28	19.7	20.3	21.0	21.7	22.5	23.2	24.0
29	18.4	19.O	19.7	20.3	21.0	21.7	22.5
30	17.3	17.8	18.4	19.0	l9.7	20.4	21.1
31	16.2	16.7	17.3	17.8	18.4	19.1	19.7
32	15.2	15.7	16.2	16.7	17.3	17.9	18.5
33	14.3	14.7	15.2	15.7	16.2	16.8	17.3
34	13.4	13.8	14.3	14.8	l5.2	15.7	16.3
35	12.6	13.0	13.4	13.9	14.3	14.8	15.3

Table 3. Ratio of total NH_4-N to NH_3-N at pH 8.0 and varying temperature and salinity

pH= 8.0 Salinity (o/oo)

T(C^O)	5	10	15	20	25	30	35
5	84.5	87.6	90.8	94.1	97.6	101.3	105.1
6	78.0	80.8	83.8	86.8	90.1	93.4	97.0
7	72.1	74.7	77.4	80.2	83.1	86.3	89.5
8	66.6	69.0	71.5	74.1	76.8	79.7	82.7
9	61.6	63.8	66.1	68.5	71.0	73.7	76.4
10	57.0	59.0	61.2	63.4	65.7	68.1	70.7
11	52.8	54.7	56.6	58.7	60.8	63.0	65.4
12	48.9	50.7	52.5	54.3	56.3	58.4	60.6
13	45.4	47.0	48.6	50.4	52.2	54.1	56.1
14	42.1	43.6	45.1	46.7	48.4	50.2	52.0
15	39.1	40.5	41.9	43.4	44.9	46.6	48.3
16	36.3	37.6	38.9	40.3	41.7	43.2	44.8
17	33.8	34.9	36.2	37.4	38.8	40.2	41.6
18	31.4	32.5	33.6	34.8	36.0	37.3	38.7
19	29.2	30.2	31.3	32.4	33.5	34.7	36.O
20	27.2	28.2	29.1	30.2	3l.2	32.3	33.5
21	25.4	26.3	27.2	28.1	29.1	30.1	31.2
22	23.7	24.5	25.3	26.2	27.1	28.1	29.1
23	22.1	22.9	23.6	24.4	25.3	26.2	27.1
24	20.7	21.3	22.1	22.8	23.6	24.4	25.3
25	19.3	19.9	20.6	21.3	22.0	22.8	23.6
26	18.1	18.7	19.3	19.9	20.6	21.3	22.1
27	16.9	17.5	18.0	18.6	19.3	19.9	20.6
28	15.8	16.4	16.9	17.5	18.0	18.7	19.3
29	14.8	15.3	15.8	16.3	16.9	17.5	18.1

30	13.9	14.4	14.8	15.3	15.8	16.4	16.9
31	13.1	13.5	13.9	14.4	14.9	15.4	15.9
32	12.3	12.7	13.1	13.5	13.9	14.4	14.9
33	11.5	11.9	12.3	12.7	13.1	13.5	14.0
34	10.9	11.2	11.6	11.9	12.3	12.7	13.1
35	10.2	10.5	10.9	11.2	11.6	12.0	12.3

Table 4. Ratio of total NH_4-N to NH_3-N at pH 8.1 and varying temperature and salinity

pH= 8.1 Salinity (o/oo)

T(C^{O})	5	10	15	20	25	30	35
5	67.4	69.8	72.3	75.0	77.7	80.7	83.7
6	62.2	64.4	66.7	69.2	71.7	74.4	77.2
7	57.5	59.5	61.7	63.9	66.3	68.7	71.3
8	53.1	55.0	57.0	59.1	61.2	63.5	65.9
9	49.1	5O.9	52.7	54.6	56.6	58.7	60.9
10	45.5	47.1	48.8	50.5	52.4	54.3	56.3
11	42.2	43.6	45.2	46.8	48.5	50.3	52.2
12	39.1	40.4	41.9	43.4	44.9	46.6	48.3
13	36.2	37.5	38.8	40.2	41.7	43.2	44.8
14	33.7	34.8	36.0	37.3	38.7	40.1	41.5
15	31.3	32.3	33.5	34.7	35.9	37.2	38.5
16	29.1	30.1	31.1	32.2	33.3	34.5	35.8
17	27.0	28.0	28.9	29.9	31.0	32.1	33.3
18	25.2	26.0	26.9	27.9	28.8	29.9	30.9
19	23.4	24.2	25.1	25.9	26.8	27.8	28.8
20	21.8	22.6	23.4	24.2	25.0	25.9	26.8
21	20.4	21.1	21.8	22.5	23.3	24.1	25.0
22	19.0	19.7	20.3	21.0	21.7	22.5	23.3
23	17.8	18.4	19.0	19.6	20.3	2l.0	21.7
24	16.6	17.2	17.7	18.3	19.0	19.6	20.3
25	15.5	16.1	16.6	17.1	17.7	18.3	19.0
26	14.0	15.0	15.5	16.0	16.6	l7.1	17.7
27	13.6	14.1	14.5	15.0	15.5	16.0	16.6
28	12.8	13.2	13.6	14.1	14.5	1520	15.5
29	12.0	12.4	12.8	13.2	13.6	14.1	14.6
30	11.3	11.6	12.0	12.4	12.8	13.2	13.7
31	10.6	10.9	11.3	11.6	12.0	12.4	12.8
32	10.0	10.3	10.6	10.9	11.3	11.6	12.0
33	9.4	9.7	10.0	10.3	10.6	11.0	11.3
34	8.8	9.1	9.4	9.7	10.0	10.3	10.6
35	8.3	8.6	8.8	9.1	9.4	9.7	10.0

Table 5. Ratio of total NH_4-N to NH_3-N at pH 8.2 and varying temperature and salinity

pH= 8.2 Salinity (o/oo)

T(C^{O})	5	10	15	20	25	30	35
5	53.7	55.6	57.6	59.7	62.0	64.3	66.7
6	49.6	51.4	53.2	55.2	57.2	59.3	61.6
7	45.8	47.5	49.2	51.0	52.8	54.8	56.8
8	42.4	43.9	45.5	47.1	48.8	50.6	52.5
9	39.2	40.6	42.1	43.6	45.2	46.8	48.6
10	36.3	37.6	39.0	40.4	41.8	43.4	45.0
11	33.7	34.9	36.l	37.4	38.7	40.1	41.6
12	31.2	32.3	33.5	34.7	35.9	37.2	38.6
13	29.O	30.0	31.1	32.2	33.3	34.5	35.8
14	26.9	27.9	28.8	29.8	30.9	32.0	33.2
15	25.0	25.9	26.8	27.7	28.7	29.7	30.8
16	23.3	24.1	24.9	25.8	26.7	27.6	28.6
17	21.7	22.4	23.2	24.0	24.8	25.7	26.6
18	20.2	20.9	21.6	22.3	23.1	23.9	24.8
19	18.8	19.5	20.1	20.8	21.5	22.3	23.1
20	17.6	18.1	18.8	19.4	20.1	20.8	21.5
21	16.4	16.9	17.5	18.1	18.7	19.4	20.0
22	15.3	15.8	16.3	16.9	17.5	18.1	18.7
23	14.3	14.8	15.3	15.8	16.3	16.9	17.5
24	13.4	13.8	14.3	14.8	15.3	15.8	16.3
25	12.6	13.3	13.4	13.8	14.3	14.8	15.3
26	11.8	12.1	12.5	12.9	13.4	13.8	14.3
27	11.0	11.4	11.7	12.1	12.5	12.9	13.4
28	10.4	10.7	11.0	11.4	11.8	12.1	12.5
29	9.7	10.0	10.4	10.7	11.0	ll.4	11.8
30	9.2	9.4	9.7	10.0	10.4	10.7	11.1
31	8.6	8.9	9.2	9.4	9.7	l0.1	10.4
32	8.1	8.4	8.6	8.9	9.2	9.5	9.8
33	7.7	7.9	8.1	8.4	8.6	8.9	9.2
34	7.2	7.4	7.7	7.9	8.1	8.4	8.7
35	6.8	7.0	7.2	7.4	7.7	7.9	8.2

Table 6. Ratio of total NH_4-N to NH_3-N at pH 8.3 and varying temperature and salinity

pH= 8.3 Salinity (o/oo)

T(C^{O})	5	10	15	20	25	30	35
5	42.9	44.4	46.0	47.7	49.4	51.3	53.2
6	39.6	41.0	42.5	44.0	45.6	47.3	49.1
7	36.6	37.9	39.3	40.7	42.2	43.7	45.4
8	33.9	35.1	36.3	37.6	39.0	40.4	41.9
9	31.4	32.5	33.6	34.8	36.1	37.4	38.8
10	29.1	30.1	31.1	32.3	33.4	34.6	35.9
11	27.0	27.9	28.9	29.9	31.0	32.1	33.3
12	25.0	25.9	26.8	27.7	28.7	29.8	30.9
13	23.2	24.0	24.9	25.7	26.7	27.6	28.6
14	21.6	22.3	23.1	23.9	24.8	25.6	26.6
15	20.1	20.8	21.5	22.2	23.0	23.8	24.7
16	18.7	19.3	20.0	20.7	21.4	22.2	23.0
17	17.4	18.0	18.6	19.3	19.9	20.6	21.4
18	16.2	16.8	17.3	17.9	18.6	19.2	19.9

19	15.2	15.7	16.2	16.7	17.3	17.9	18.5
20	14.2	14.6	15.1	15.6	16.1	16.7	17.3
21	13.2	13.7	14.1	14.6	15.1	15.6	16.1
22	12.4	12.8	13.2	13.6	14.1	14.6	15.1
23	11.6	12.0	12.3	12.7	13.2	13.6	14.1
24	10.9	11.2	11.6	11.9	12.3	12.7	l3.2
25	10.2	l0.5	10.8	11.2	11.5	11.9	12.3
26	9.6	9.8	10.2	10.5	10.8	11.2	11.6
27	9.0	9.2	9.5	9.8	10.2	10.5	10.8
28	8.4	8.7	9.0	9.2	9.5	9.8	10.2
29	7.9	8.2	8.4	8.7	9.0	9.3	9.5
30	7.5	7.7	7.9	8.2	8.4	8.7	9.0
31	7.1	7.3	7.5	7.7	7.9	8.2	8.5
32	6.7	6.8	7.1	7.3	7.5	7.7	8.0
33	6.3	6.5	6.7	6.9	7.1	7.3	7.5
34	5.9	6.1	6.3	6.5	6.7	6.9	7.1
35	5.6	5.8	5.9	6.1	6.3	6.5	6.7