# SUPPLEMENTARY INFORMATION

# FIRST ACID IONIZATION CONSTANT OF THE DRINKING WATER RELEVANT CHEMICAL CYANURIC ACID FROM 5 TO 35 °C

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**Summary: Supporting information consists of 8 pages containing a description of the derivation of Equations 4 and 5, correction of O'Brien, *et al.*[1] $pK_6$ to $\mu = 0$ M, 2 figures, 2 tables, and associated references.**

**Derivation of Equations 4 and 5**

From Equations 2 and 3, Equations 4 and 5 represent the concentration fraction of TOTCy that is $H_3Cy$ ($\alpha_0$) or $H_2Cy^-$ ($\alpha_1$), respectively.

$$K_{6,T_K} = \frac{\{H_2Cy^-\}\{H^+\}}{\{H_3Cy\}} = \frac{\gamma_1[H_2Cy^-]\{H^+\}}{[H_3Cy]} \quad (2)$$

$$[TOTCy] = [H_3Cy] + [H_2Cy^-] \quad (3)$$

$$\alpha_0 = \frac{[H_3Cy]}{[TOTCy]} = \frac{[H_3Cy]}{[H_3Cy] + [H_2Cy^-]} = \frac{1}{1 + \frac{[H_2Cy^-]}{[H_3Cy]}} = \frac{1}{1 + \frac{K_{6,T_K}}{\gamma_1\{H^+\}}} = \frac{\gamma_1\{H^+\}}{\gamma_1\{H^+\} + K_{6,T_K}} \quad (4)$$

$$\alpha_1 = \frac{[H_2Cy^-]}{[TOTCy]} = \frac{[H_2Cy^-]}{[H_3Cy] + [H_2Cy^-]} = \frac{1}{\frac{[H_3Cy]}{[H_2Cy^-]} + 1} = \frac{1}{\frac{\gamma_1\{H^+\}}{K_{6,T_K}} + 1} = \frac{K_{6,T_K}}{\gamma_1\{H^+\} + K_{6,T_K}} \quad (5)$$

**Adjustment of O'Brien, *et al.*[1] p$K_6$ estimate to $\mu$ = 0 M**

O'Brien, *et al.*[1] determined their p$K_6$ at $\mu$ = 20 mM which corresponds to a calculated $\gamma_1$ of 0.868, using Equation 8 at 25 °C. O'Brien, *et al.*[1] used $\{H^+\}$ and concentration to determine $K_6$; therefore, their determined $K_6$ is represented by Equation S1 ($K_{6,20\ mM}$). The corresponding activity based $K_6$ is represented by Equation S2. Substituting Equation S1 into Equation S2, results in Equation S3 which allows calculation of $K_6$ at $\mu$ = 0 M (p$K_6$ = 6.94).

$$K_{6,20\ mM} = \frac{[H_2Cy^-]\{H^+\}}{[H_3Cy]} = 10^{-6.88} \tag{S1}$$

$$K_6 = \frac{\{H_2Cy^-\}\{H^+\}}{\{H_3Cy\}} = \frac{\gamma_1[H_2Cy^-]\{H^+\}}{[H_3Cy]} \tag{S2}$$

$$K_6 = \frac{\gamma_1[H_2Cy^-]\{H^+\}}{[H_3Cy]} = (\gamma_1)(K_{6,20\ mM}) = (0.868)(10^{-6.88}) = 10^{-6.94} \tag{S3}$$

**Table S1 – Multiple comparison summary of molar absorptivity estimates at various temperatures. Boxes with diagonal crosses indicate a significant difference whereas empty, white boxes do not indicate a significant difference between molar absorptivity estimates.**

**Cyanuric Acid ($H_3Cy$) Molar Absorptivity Estimate Comparison Summary (pH = 1.82 ± 0.057)**

| **Temperature – °*C*** | 5.2 | 10.2 | 15.7 | 19.2 | 24.5 | 30.0 | 34.0 |
|---|---|---|---|---|---|---|---|
| 5.2 | | | | | | | |
| 10.2 | X | | | | | | |
| 15.7 | X | | | | | | |
| 19.2 | X | | X | | | | |
| 24.5 | X | | | X | | | |
| 30.0 | X | X | X | X | X | | |
| 34.0 | X | | | X | | X | |

**Cyanuric Acid First Ionization Product ($H_2Cy^-$) Molar Absorptivity Estimate Comparison Summary (pH = 9.00 ± 0.010 unless noted by * then pH = 9.51 ± 0.0092)**

| **Temperature – °*C*** | 5.2* | 5.0 | 10.4* | 10.2 | 16.0 | 19.4 | 24.2 | 30.5 | 34.7 |
|---|---|---|---|---|---|---|---|---|---|
| 5.2* | | | | | | | | | |
| 5.0 | | | | | | | | | |
| 10.4* | X | X | | | | | | | |
| 10.2 | | X | | | | | | | |
| 16.0 | X | X | | | | | | | |
| 19.4 | X | X | X | X | X | | | | |
| 24.2 | X | X | X | X | X | X | | | |
| 30.5 | | | X | X | X | X | X | | |
| 34.7 | X | X | X | X | X | X | X | X | |

## Table S2 – Experimental data summary (126 total data points).

| T – °*C* | Exp | pH | Abs | IS – *M* | $\gamma_1$ |
|---|---|---|---|---|---|
| 5.4 ± 0.29 | A | 6.01 | 0.064 | 4.14E-03 | 0.934 |
| | A | 6.50 | 0.163 | 4.37E-03 | 0.933 |
| | A | 7.01 | 0.383 | 4.84E-03 | 0.929 |
| | A | 7.50 | 0.701 | 5.39E-03 | 0.926 |
| | A | 8.01 | 0.978 | 5.76E-03 | 0.924 |
| | A | 8.51 | 1.114 | 5.95E-03 | 0.923 |
| | B | 5.99 | 0.062 | 4.13E-03 | 0.934 |
| | B | 6.49 | 0.155 | 4.36E-03 | 0.933 |
| | B | 7.00 | 0.368 | 4.83E-03 | 0.930 |
| | B | 7.50 | 0.693 | 5.39E-03 | 0.926 |
| | B | 8.00 | 0.974 | 5.76E-03 | 0.924 |
| | B | 8.50 | 1.118 | 5.95E-03 | 0.923 |
| | C | 6.01 | 0.066 | 4.14E-03 | 0.934 |
| | C | 6.51 | 0.161 | 4.37E-03 | 0.933 |
| | C | 7.01 | 0.385 | 4.84E-03 | 0.929 |
| | C | 7.50 | 0.701 | 5.39E-03 | 0.926 |
| | C | 8.01 | 0.980 | 5.76E-03 | 0.924 |
| | C | 8.51 | 1.121 | 5.95E-03 | 0.923 |
| 10.4 ± 0.23 | A | 6.00 | 0.078 | 4.14E-03 | 0.934 |
| | A | 6.50 | 0.197 | 4.37E-03 | 0.932 |
| | A | 7.02 | 0.460 | 4.87E-03 | 0.929 |
| | A | 7.50 | 0.792 | 5.40E-03 | 0.925 |
| | A | 8.00 | 1.059 | 5.76E-03 | 0.923 |
| | A | 8.48 | 1.188 | 5.95E-03 | 0.922 |
| | B | 6.00 | 0.077 | 4.14E-03 | 0.934 |
| | B | 6.50 | 0.198 | 4.37E-03 | 0.932 |
| | B | 6.99 | 0.442 | 4.84E-03 | 0.929 |
| | B | 7.51 | 0.797 | 5.41E-03 | 0.925 |
| | B | 7.99 | 1.058 | 5.76E-03 | 0.923 |
| | B | 8.50 | 1.191 | 5.95E-03 | 0.922 |
| | C | 6.00 | 0.078 | 4.14E-03 | 0.934 |
| | C | 6.51 | 0.201 | 4.38E-03 | 0.932 |
| | C | 7.01 | 0.449 | 4.86E-03 | 0.929 |
| | C | 7.49 | 0.788 | 5.39E-03 | 0.926 |
| | C | 8.00 | 1.064 | 5.76E-03 | 0.923 |
| | C | 8.50 | 1.194 | 5.95E-03 | 0.922 |
| 16.5 ± 0.37 | A | 6.01 | 0.101 | 4.14E-03 | 0.933 |
| | A | 6.49 | 0.244 | 4.38E-03 | 0.931 |
| | A | 7.00 | 0.534 | 4.86E-03 | 0.928 |
| | A | 7.50 | 0.869 | 5.42E-03 | 0.925 |
| | A | 8.00 | 1.086 | 5.77E-03 | 0.923 |
| | A | 8.50 | 1.182 | 5.96E-03 | 0.921 |
| | B | 5.99 | 0.099 | 4.14E-03 | 0.933 |
| | B | 6.50 | 0.251 | 4.38E-03 | 0.931 |
| | B | 6.99 | 0.536 | 4.85E-03 | 0.928 |
| | B | 7.51 | 0.880 | 5.43E-03 | 0.925 |
| | B | 8.00 | 1.106 | 5.77E-03 | 0.923 |
| | B | 8.51 | 1.209 | 5.96E-03 | 0.921 |
| | C | 6.02 | 0.104 | 4.15E-03 | 0.933 |
| | C | 6.51 | 0.257 | 4.39E-03 | 0.931 |
| | C | 7.01 | 0.552 | 4.88E-03 | 0.928 |
| | C | 7.50 | 0.879 | 5.42E-03 | 0.925 |
| | C | 7.99 | 1.108 | 5.77E-03 | 0.923 |
| | C | 8.51 | 1.213 | 5.96E-03 | 0.921 |
| 19.8 ± 0.37 | A | 6.00 | 0.104 | 4.14E-03 | 0.933 |
| | A | 6.51 | 0.263 | 4.40E-03 | 0.931 |
| | A | 7.01 | 0.542 | 4.88E-03 | 0.928 |
| | A | 7.50 | 0.825 | 5.42E-03 | 0.924 |
| | A | 8.01 | 0.991 | 5.78E-03 | 0.922 |
| | A | 8.48 | 1.054 | 5.96E-03 | 0.921 |
| | B | 6.00 | 0.113 | 4.14E-03 | 0.933 |
| | B | 6.51 | 0.282 | 4.40E-03 | 0.931 |
| | B | 6.99 | 0.533 | 4.86E-03 | 0.928 |
| 19.8 ± 0.37 | B | 7.51 | 0.838 | 5.43E-03 | 0.924 |
| | B | 8.00 | 1.000 | 5.77E-03 | 0.922 |
| | B | 8.51 | 1.073 | 5.97E-03 | 0.921 |
| | C | 6.00 | 0.109 | 4.14E-03 | 0.933 |
| | C | 6.51 | 0.270 | 4.40E-03 | 0.931 |
| | C | 6.99 | 0.541 | 4.86E-03 | 0.928 |
| | C | 7.51 | 0.837 | 5.43E-03 | 0.924 |
| | C | 8.00 | 1.005 | 5.77E-03 | 0.922 |
| | C | 8.51 | 1.074 | 5.97E-03 | 0.921 |
| 24.8 ± 0.33 | A | 6.00 | 0.115 | 4.15E-03 | 0.932 |
| | A | 6.49 | 0.284 | 4.39E-03 | 0.930 |
| | A | 7.01 | 0.589 | 4.90E-03 | 0.927 |
| | A | 7.49 | 0.869 | 5.43E-03 | 0.924 |
| | A | 7.99 | 1.032 | 5.78E-03 | 0.921 |
| | A | 8.49 | 1.101 | 5.96E-03 | 0.920 |
| | B | 6.01 | 0.121 | 4.15E-03 | 0.932 |
| | B | 6.50 | 0.292 | 4.40E-03 | 0.930 |
| | B | 6.99 | 0.577 | 4.87E-03 | 0.927 |
| | B | 7.50 | 0.873 | 5.44E-03 | 0.923 |
| | B | 7.99 | 1.038 | 5.78E-03 | 0.921 |
| | B | 8.48 | 1.106 | 5.96E-03 | 0.920 |
| | C | 6.00 | 0.120 | 4.15E-03 | 0.932 |
| | C | 6.51 | 0.302 | 4.41E-03 | 0.930 |
| | C | 7.01 | 0.598 | 4.90E-03 | 0.927 |
| | C | 7.50 | 0.882 | 5.44E-03 | 0.923 |
| | C | 7.99 | 1.050 | 5.78E-03 | 0.921 |
| | A | 6.00 | 0.115 | 4.15E-03 | 0.932 |
| 30.7 ± 0.17 | A | 6.01 | 0.157 | 4.15E-03 | 0.931 |
| | A | 6.50 | 0.372 | 4.41E-03 | 0.929 |
| | A | 7.01 | 0.707 | 4.91E-03 | 0.926 |
| | A | 7.51 | 0.978 | 5.46E-03 | 0.923 |
| | A | 8.01 | 1.119 | 5.79E-03 | 0.921 |
| | A | 8.49 | 1.172 | 5.97E-03 | 0.919 |
| | B | 6.01 | 0.163 | 4.15E-03 | 0.931 |
| | B | 6.51 | 0.388 | 4.42E-03 | 0.929 |
| | B | 7.01 | 0.726 | 4.91E-03 | 0.926 |
| | B | 7.50 | 0.998 | 5.45E-03 | 0.923 |
| | B | 8.01 | 1.148 | 5.79E-03 | 0.921 |
| | B | 8.50 | 1.203 | 5.97E-03 | 0.919 |
| | C | 6.01 | 0.167 | 4.15E-03 | 0.931 |
| | C | 6.49 | 0.380 | 4.40E-03 | 0.930 |
| | C | 7.00 | 0.725 | 4.90E-03 | 0.926 |
| | C | 7.50 | 1.005 | 5.45E-03 | 0.923 |
| | C | 7.99 | 1.150 | 5.78E-03 | 0.921 |
| | C | 8.50 | 1.210 | 5.97E-03 | 0.919 |
| 34.4 ± 0.086 | A | 5.99 | 0.150 | 4.15E-03 | 0.931 |
| | A | 6.50 | 0.358 | 4.41E-03 | 0.929 |
| | A | 7.00 | 0.659 | 4.91E-03 | 0.926 |
| | A | 7.49 | 0.901 | 5.45E-03 | 0.922 |
| | A | 7.99 | 1.025 | 5.79E-03 | 0.920 |
| | A | 8.50 | 1.074 | 5.98E-03 | 0.919 |
| | B | 6.00 | 0.154 | 4.15E-03 | 0.931 |
| | B | 6.51 | 0.372 | 4.42E-03 | 0.929 |
| | B | 6.99 | 0.668 | 4.90E-03 | 0.926 |
| | B | 7.51 | 0.922 | 5.46E-03 | 0.922 |
| | B | 8.01 | 1.044 | 5.79E-03 | 0.920 |
| | B | 8.50 | 1.092 | 5.98E-03 | 0.919 |
| | C | 6.01 | 0.166 | 4.16E-03 | 0.931 |
| | C | 6.50 | 0.381 | 4.41E-03 | 0.929 |
| | C | 6.99 | 0.685 | 4.90E-03 | 0.926 |
| | C | 7.51 | 0.943 | 5.46E-03 | 0.922 |
| | C | 7.99 | 1.064 | 5.79E-03 | 0.920 |
| | C | 8.50 | 1.114 | 5.98E-03 | 0.919 |

**Abs – Absorbance at 214 nm, Exp – Experiment, IS – Ionic strength, T – Average Temperature ± Standard Deviation, $\gamma_1$ – Activity Coefficient**

**Figure S1 – Free chlorine, cyanuric acid, and chlorinated cyanurate equilibria. Grey highlighted chemicals are the major cyanurate containing species expected under drinking water conditions and chemical dosages. Hydrogen ion for dissociation reactions and water and hypochlorous acid for hydrolysis reactions are not shown for clarity. Adapted with permission from Brady, *et al.*[2]. Copyright 1963 American Chemical Society.**

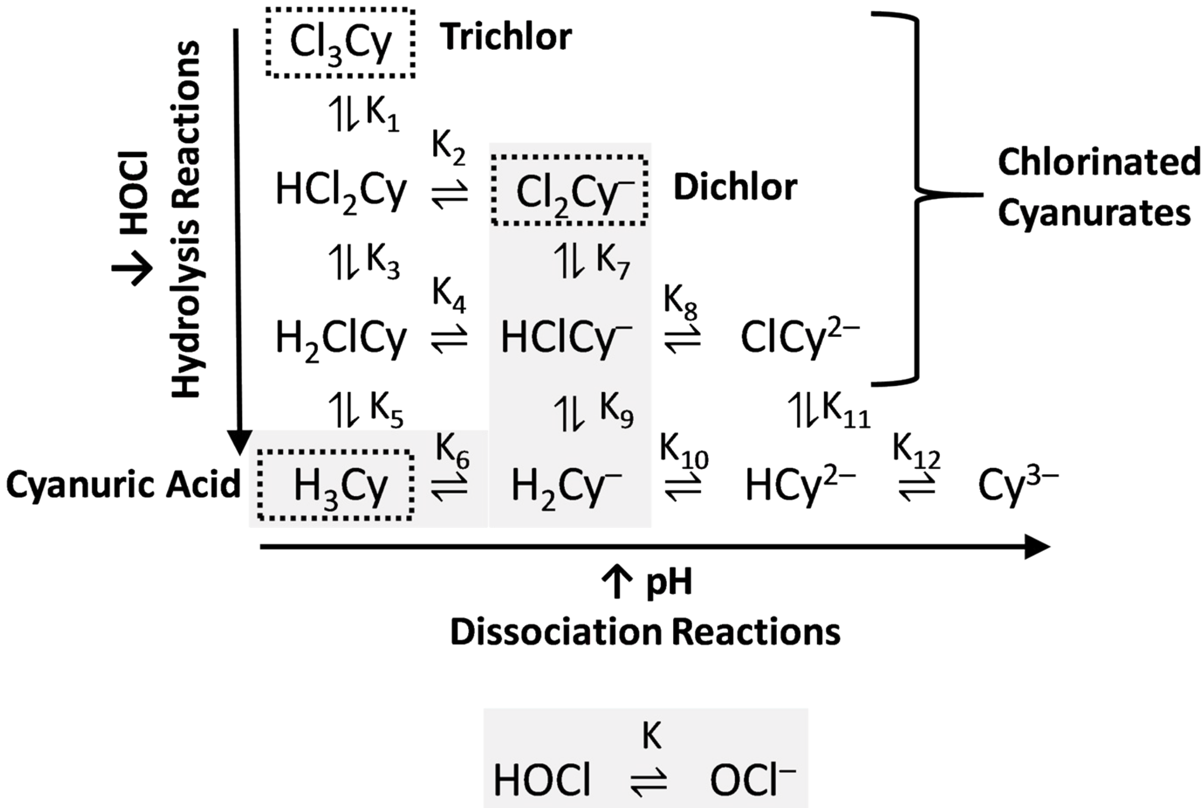
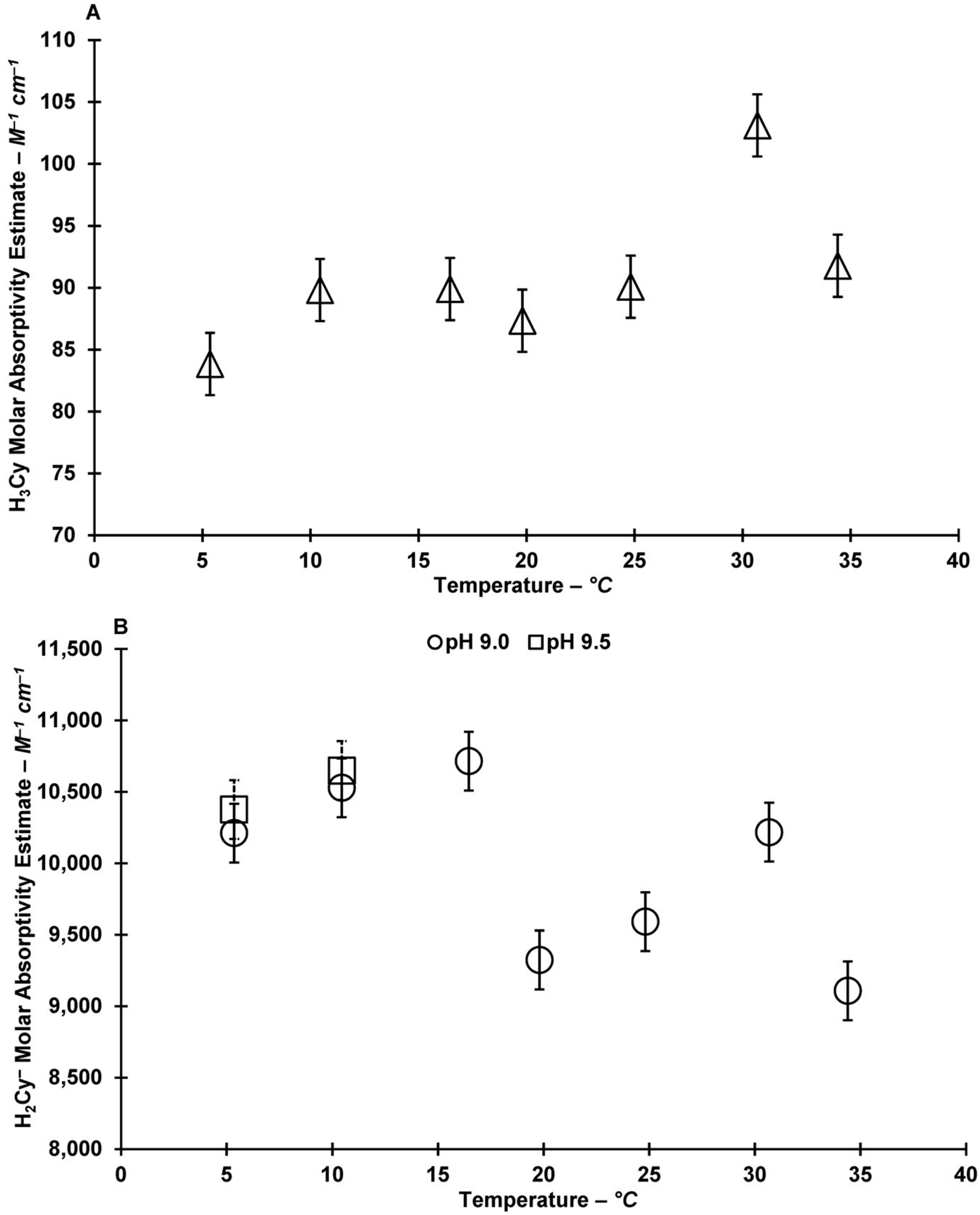


**Figure S2 – Molar absorptivity estimates for cyanuric acid ($H_3Cy$, A) and its first ionization product ($H_2Cy^-$, B). Bars represent the 95% confidence interval from Tukey's multiple comparison statistic calculated using Equation 1.**



## REFERENCES

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2. A. P. Brady, K. M. Sancier and G. Sirine, Equilibria in Solutions of Cyanuric Acid and its Chlorinated Derivatives, *J. Am. Chem. Soc.*, 1963, **85**, 3101–3104.