EPA
United States
Environmental Protection
Agency

EPA/600/S-17/165
June 2017
www.epa.gov/research

Free Chlorine and Cyanuric Acid Simulator Application Description - Version 0.50

Office of Research and Development
National Risk Management Research Laboratory
Water Systems Division

Free Chlorine and Cyanuric Acid Simulator

Application Description – Version 0.50 – May 10, 2017

INTRODUCTION

A web–based application (WBA) has been developed to simulate the water chemistry associated with the free chlorine and cyanuric acid system (i.e., chlorinated cyanurates). The WBA can be accessed at https://usepaord.shinyapps.io/cyanuric/ (all lowercase).

The WBA is freely accessible, providing drinking water practitioners (e.g., operators, regulators, engineers, professors, and students) a tool to explore the water chemistry of the free chlorine and cyanuric acid system and to estimate free chlorine concentrations in an interactive manner without requiring proprietary software or modeling expertise. The WBA allows the user to specify two side–by–side simulations, providing a direct comparison of impacts associated with changing initial conditions (e.g., free chlorine, cyanuric acid, Dichlor, and Trichlor concentrations and pH). Once completed, the user may download simulation data to use offline.

The WBA allows the user to estimate the free chlorine concentration when cyanuric acid is present as is the case when adding chlorine–containing chemicals commonly referred to as Dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) or Trichlor (trichloroisocyanuric acid) to drinking water systems. The tool is based on the equilibrium model presented by O'Brien (1972) and O'Brien et al (1974) for 25°C. Note that currently no information is available at temperatures other than 25°C, and the user must be aware of this fact when operating at different temperatures as simulated concentration may differ.

FREE CHLORINE AND CYANURIC ACID APPLICATION

The WBA is self–contained and provides the necessary information to direct the user on how to conduct a simulation, providing guidance through pop–up boxes that appear when hovering a screen pointer over a required input or possible selection (Figure 1).

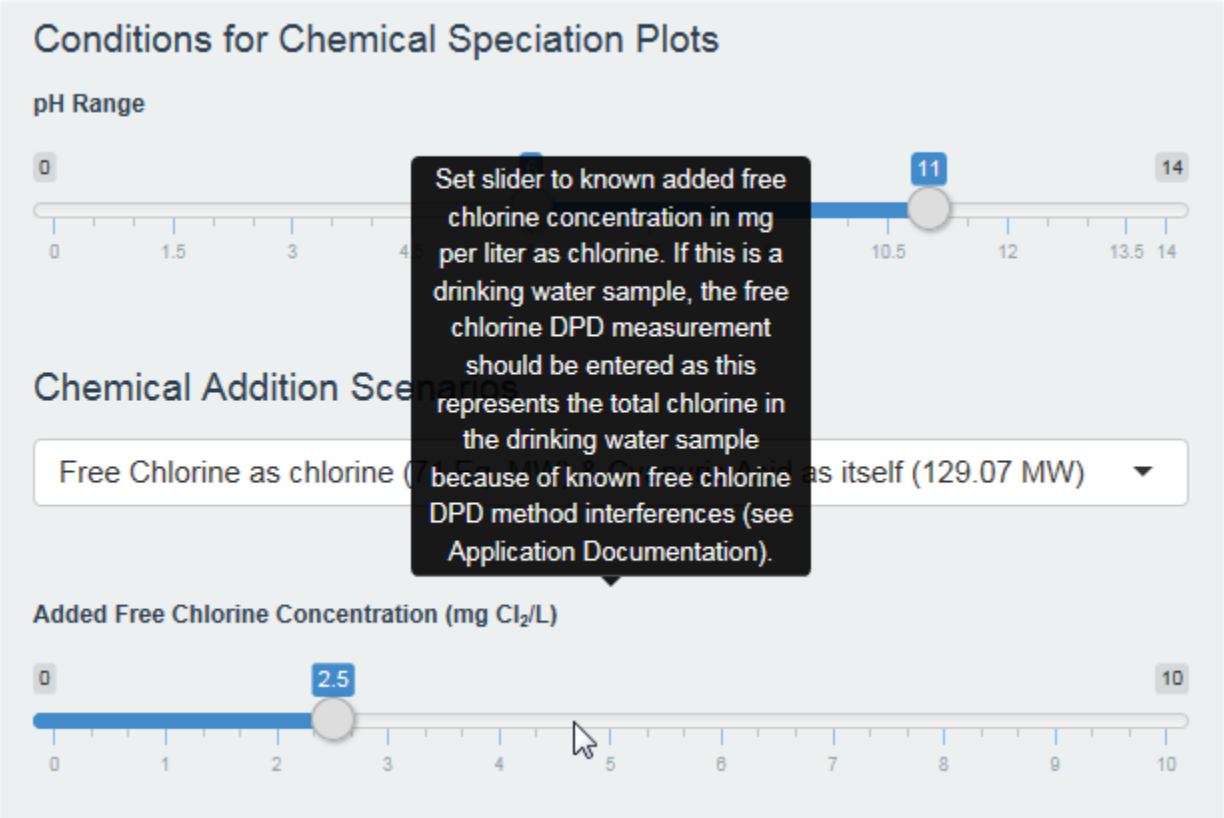

Figure 1 Example tooltip pop–up box

The WBA consists of several areas described below in detail: header, simulation input, plot preferences, and output plot.

Header area. The top of the WBA's web page contains a header area (Figure 2) where general information about the WBA is presented along with hyperlinks to the main research article used in creating the WBA and the Application Documentation (i.e., this document).

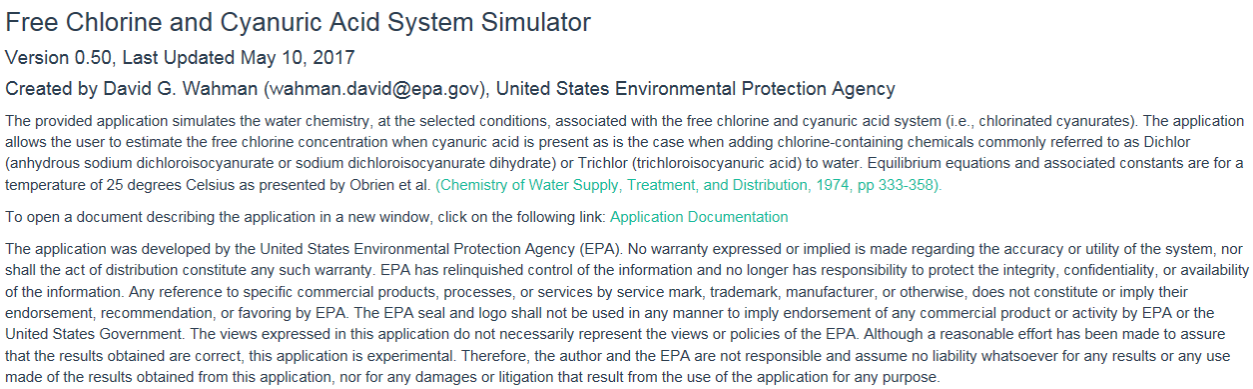

Figure 2 Header area

Simulation input area. Below the header area is the simulation input area where the user selects and inputs the desired variables required to conduct simulations (Figure 3). In the simulation input area, the user selects the simulation pH range. The default range is set to pH 6 to 11, representing a range that would cover drinking water, but the user is free to select any range from pH 0 to 14 to further explore the water chemistry.

The user may select from seven different chemical addition scenarios which correlate to the chemical speciation immediately after adding the following combination of chemicals to water without accounting for any chlorine demand present in the water:

1. Free chlorine as chlorine and cyanuric acid as itself,
2. Anhydrous sodium dichloroisocyanurate as chlorine,
3. Anhydrous sodium dichloroisocyanurate as itself,
4. Sodium dichloroisocyanurate dihydrate as chlorine,
5. Sodium dichloroisocyanurate dihydrate as itself,
6. Trichloroisocyanuric acid as chlorine, or
7. Trichloroisocyanuric acid as itself.

Depending on the scenario selected, the options for entering chemical concentrations will change accordingly. When entering chemical concentrations "as itself", the WBA assumes that the chemical has a 100% purity. For each chemical addition scenario, the WBA uses the entered chemical concentrations to determine the total chlorine (TOTCl) and total cyanurate (TOTCy) concentrations to use in the simulations.

In addition to simulating the immediate speciation after direct addition of the various chemicals, the free chlorine and cyanuric acid scenario can also be used to simulate conditions and estimate the free chlorine concentration for water samples where chlorine demand has decreased the initial amount of TOTCl added to the water. In this case, the free chlorine concentration entered is the measured free chlorine concentration obtained from the free chlorine DPD (e.g., HACH Company, 2014a) or amperometric titration (APHA et al, 2005) methods which will actually provide the TOTCl concentration in the water because of known method interferences (Wajon & Carrell Morris, 1980; Whittle, 1970). The user will also need to know or estimate the TOTCy concentration where the sample was taken to enter in for the cyanuric acid concentration.

In drinking water, TOTCy concentrations are generally less than the available method detection limit of simple field kits (approximately 5 mg/L) which rely on melamine precipitation chemistry (HACH Company, 2014b). Currently, other methods exist that could be used to measure cyanuric acid concentrations at drinking water relevant concentrations, but they are complex and include silver nanoparticles (Kappi et al, 2014), high performance liquid chromatography (Hou & Ding, 2011; Sun et al, 2011; Downes et al, 1984; Briggle et al, 1981), differential pulse polarography (Struys & Wolfs, 1987), and ultraviolet detection (Downes et al,

1984). Therefore, the TOTCy concentration cannot be measured currently at concentrations expected in typical drinking water samples in the field.

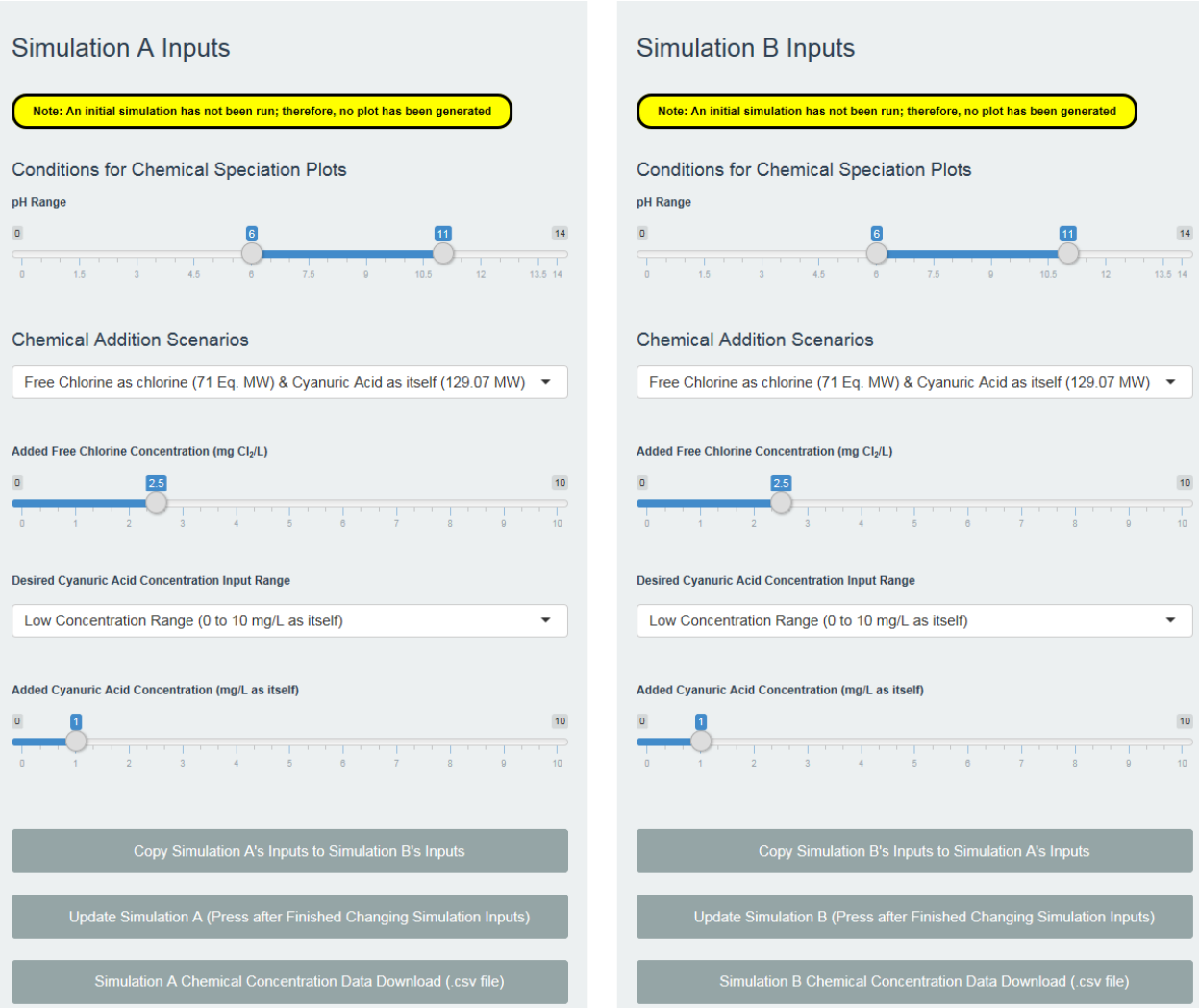

Figure 3 Simulation input area

As opposed to TOTCl which will decrease due to the water's chlorine demand and must be measured directly, TOTCy should be relatively stable in drinking water. Therefore, the TOTCy concentration may be estimated conservatively by the user from the original dosage of cyanurate containing chemicals added to the water, requiring the user to know the dosage and

appropriately calculate the added TOTCy. To serve as a guide, the TOTCy added as cyanuric acid for each 1 mg/L of the three chemicals approved for use in drinking water and cyanuric acid is summarized in Table 1, assuming 100% chemical purity.

Table 1 Total cyanurate (TOTCy) addition for each 1 mg/L of chemical addition

Chemical Added as Itself	Molecular Weight	Total Cyanuric (TOTCy) Addition as Cyanuric Acid (mg/L) for each mg/L of Chemical Added as Itself
Cyanuric Acid	129.07	1.000
Anhydrous Sodium Dichloroisocyanurate	219.95	0.587
Sodium Dichloroisocyanurate Dihydrate	255.98	0.504
Trichloroisocyanuric Acid	232.41	0.555

The simulation input area also contains three buttons that allow the user to (1) copy the current simulation's input conditions directly to the other simulation (*Copy Simulation A's Inputs to Simulation B's Inputs*), (2) run the simulation with the provided input conditions and generate output plots (*Update Simulation A and Plots [Press after Finishing Changing Simulation Inputs*]), and (3) export the finished simulation data to a comma–separated variable (.csv) file for use in external programs (*Simulation A Chemical Concentration Data Download [.csv file]*).

Plot preferences area. After entering the conditions and running a simulation, the WBA's next area allows the user to select the Y–axis ranges (Figure 4) for the concentration plots (Figure 5). For the two log concentration plots (i.e., the top two plots in Figure 5), a range of 1 to 20 log units is provided. For the mg/L concentration plot (i.e., the bottom plot in Figure 5), the user can select the lower and upper limits on the Y–axis based on a percentage of the TOTCl. The default is the range of 0–100% which displays the entire TOTCl range, but the user can narrow this range to focus in on areas of the mg/L concentration plot as desired to see

additional detail. Once the user completes the selections, the user may press the *Update Plots for Simulation A* (or *B*) button to immediately update the plots to adjust the Y–axis range displayed.

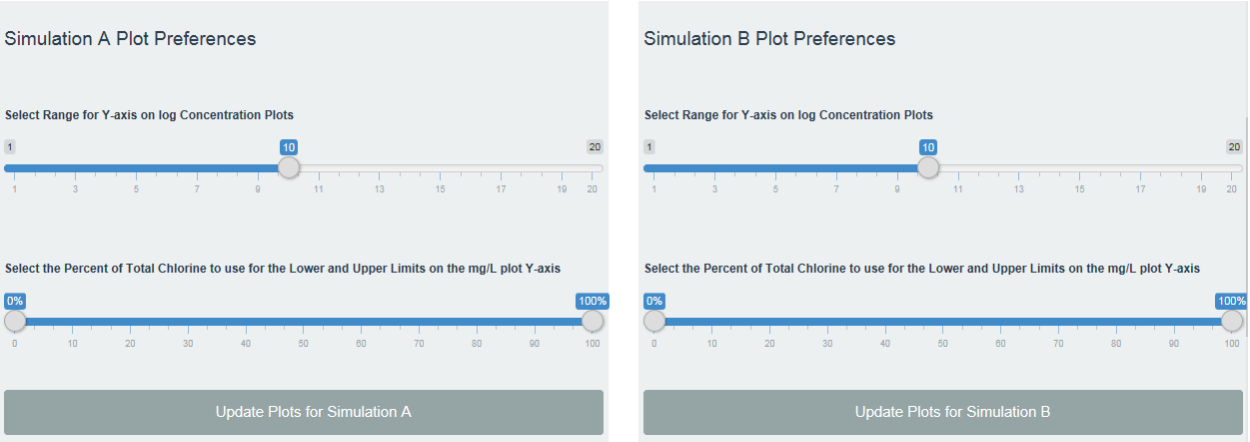

Figure 4 Plot preferences area

Output plot area. The WBA generates three plots for each simulation (Figure 5). The first plot displays a log concentration plot versus pH for all the chemical species simulated. The second plot produces a plot similar to the first but only includes those species that contain chlorine and presents the concentrations as the log mg/L as Cl_2. The third plot focuses in on free chlorine by displaying TOTCl, free chlorine, hypochlorous acid (HOCl), and hypochlorite ion (OCl^-) concentrations as mg/L as Cl_2.

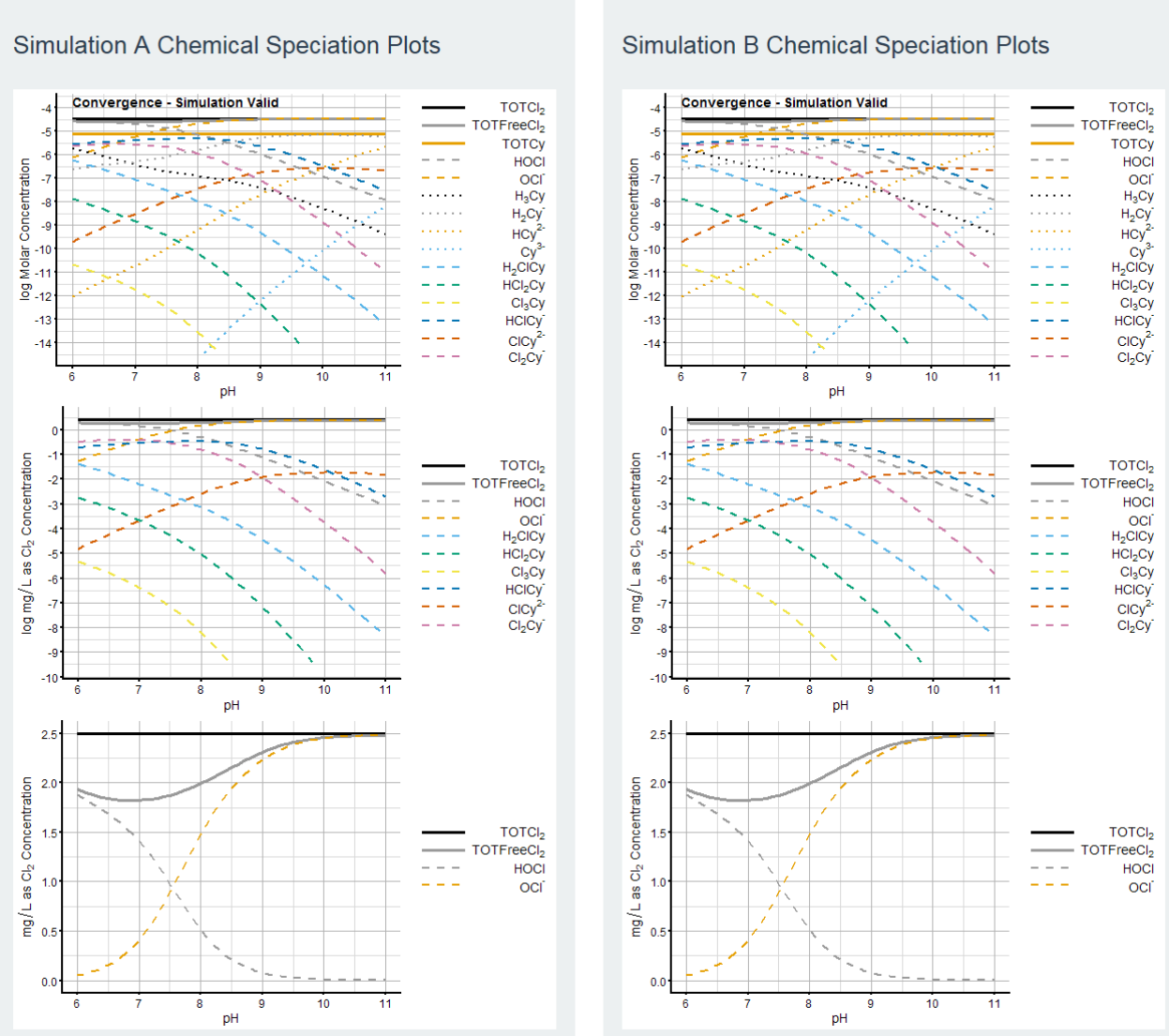

Figure 5 Output plot area

MODEL IMPLEMENTATION

The required chemical reactions and associated equilibrium constants required to simulate the water chemistry of the free chlorine and cyanuric acid system are presented in Table 2. To simulate the water chemistry, TOTCl, TOTCy, and pH (which provides the hydrogen ion, H^+, concentration) must be known or assumed (Figure 6). With these three known concentrations, there are twelve remaining unknown concentrations, which require twelve independent equations

(Eq 1 through Eq 12, Figure 6) to provide a unique solution for the system. Using the twelve equations (Eqs 1 through 12), a single working equation where only the HOCl concentration is unknown can be derived (Eq 15, Figure 7). For each pH, the WBA (i) solves Eq 15 for the HOCl concentration, (ii) uses the determined HOCl concentration to solve Eqs 12 and 13 for the cyanurate ion (Cy^{3-}) and OCl^- concentrations, and (iii) uses the determined Cy^{3-} concentration to solve Eqs 3 through 11 for the remaining nine unknown chemical concentrations. Please note that "Cy" represents a shorthand notation of the cyanurate structure which has the chemical formula of $C_3N_3O_3$.

Table 2 Required equilibrium reactions and constants to simulate water chemistry

Reaction	Constant	pK [a]
$Cl_3Cy \rightleftharpoons HCl_2Cy + HOCl$	K_{1a}	1.8
$HCl_2Cy \rightleftharpoons Cl_2Cy^- + H^+$	K_2	3.75
$H_2ClCy \rightleftharpoons HClCy^- + H^+$	K_4	5.33
$H_3Cy \rightleftharpoons H_2Cy^- + H^+$	K_6	6.88
$Cl_2Cy^- \rightleftharpoons HClCy^- + HOCl$	K_{7a}	4.51
$HClCy^- \rightleftharpoons ClCy^{2-} + H^+$	K_8	10.12
$H_2Cy^- \rightleftharpoons HCy^{2-} + H^+$	K_{10}	11.40
$ClCy^{2-} \rightleftharpoons HCy^{2-} + HOCl$	K_{11a}	6.90
$HCy^{2-} \rightleftharpoons Cy^{3-} + H^+$	K_{12}	13.5
$HOCl \rightleftharpoons OCl^- + H^+$	K	7.54 [b]

[a] O'Brien et al (1974) unless otherwise noted

[b] Morris (1966)

Assumed Knowns (3)

$TOTCl, TOTCy, [H^+]$

Remaining Unknowns (12)

$[Cl_3Cy], [HCl_2Cy], [H_2ClCy], [Cl_2Cy^-], [HClCy^-], [ClCy^{2-}], [H_3Cy], [H_2Cy^-], [HCy^{2-}], [Cy^{3-}], [HOCl], [OCl^-]$

Required Equations (12)

$$TOTCl = 3[Cl_3Cy] + 2[HCl_2Cy] + [H_2ClCy] + 2[Cl_2Cy^-] + [HClCy^-] + [ClCy^{2-}] + [HOCl] + [OCl^-] \quad (1)$$

$$TOTCy = [Cl_3Cy] + [HCl_2Cy] + [H_2ClCy] + [Cl_2Cy^-] + [HClCy^-] + [ClCy^{2-}] + [H_3Cy] + [H_2Cy^-] + [HCy^{2-}] + [Cy^{3-}] \quad (2)$$

$$\frac{[H^+][Cy^{3-}]}{[HCy^{2-}]} = K_{12} \qquad [HCy^{2-}] = \frac{[H^+][Cy^{3-}]}{K_{12}} \quad (3)$$

$$\frac{[H^+][HCy^{2-}]}{[H_2Cy^-]} = K_{10} \qquad \frac{[H^+][H^+][Cy^{3-}]}{[H_2Cy^-]K_{12}} = K_{10} \qquad [H_2Cy^-] = \frac{[H^+]^2[Cy^{3-}]}{K_{12}K_{10}} \quad (4)$$

$$\frac{[H^+][H_2Cy^-]}{[H_3Cy]} = K_6 \qquad \frac{[H^+][H^+]^2[Cy^{3-}]}{K_{12}K_{10}[H_3Cy]} = K_6 \qquad [H_3Cy] = \frac{[H^+]^3[Cy^{3-}]}{K_{12}K_{10}K_6} \quad (5)$$

$$\frac{[HOCl][HCy^{2-}]}{[ClCy^{2-}]} = K_{11a} \qquad \frac{[H^+][HOCl][Cy^{3-}]}{K_{12}[ClCy^{2-}]} = K_{11a} \qquad [ClCy^{2-}] = \frac{[H^+][HOCl][Cy^{3-}]}{K_{12}K_{11a}} \quad (6)$$

$$\frac{[H^+][ClCy^{2-}]}{[HClCy^-]} = K_8 \qquad \frac{[H^+][H^+][HOCl][Cy^{3-}]}{K_{12}K_{11a}[HClCy^-]} = K_8 \qquad [HClCy^-] = \frac{[H^+]^2[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8} \quad (7)$$

$$\frac{[H^+][HClCy^-]}{[H_2ClCy]} = K_4 \qquad \frac{[H^+][H^+]^2[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8[H_2ClCy]} = K_4 \qquad [H_2ClCy] = \frac{[H^+]^3[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8K_4} \quad (8)$$

$$\frac{[HOCl][HClCy^-]}{[Cl_2Cy^-]} = K_{7a} \qquad \frac{[HOCl][H^+]^2[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8[Cl_2Cy^-]} = K_{7a} \qquad [Cl_2Cy^-] = \frac{[H^+]^2[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}} \quad (9)$$

$$\frac{[H^+][Cl_2Cy^-]}{[HCl_2Cy]} = K_2 \qquad \frac{[H^+][H^+]^2[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}[HCl_2Cy]} = K_2 \qquad [HCl_2Cy] = \frac{[H^+]^3[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2} \quad (10)$$

$$\frac{[HOCl][HCl_2Cy]}{[Cl_3Cy]} = K_{1a} \qquad \frac{[HOCl][H^+]^3[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2[Cl_3Cy]} = K_{1a} \qquad [Cl_3Cy] = \frac{[H^+]^3[HOCl]^3[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} \quad (11)$$

$$\frac{[H^+][OCl^-]}{[HOCl]} = K \qquad [OCl^-] = \frac{K[HOCl]}{[H^+]} \quad (12)$$

Figure 6 System of twelve equations required to solve water chemistry

Step 1 – Solution of TOTCl in terms of Cy^{3-} (Eq. 13)

$$TOTCl = 3[Cl_3Cy] + 2[HCl_2Cy] + [H_2ClCy] + 2[Cl_2Cy^-] + [HClCy^-] + [ClCy^{2-}] + [HOCl] + [OCl^-]$$

$$TOTCl = 3\frac{[H^+]^3[HOCl]^3[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + 2\frac{[H^+]^3[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8K_4} + 2\frac{[H^+]^2[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl][Cy^{3-}]}{K_{12}K_{11a}} + [HOCl] + \frac{K[HOCl]}{[H^+]}$$

$$TOTCl = [Cy^{3-}]\left(3\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + 2\frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2\frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}\right) + [HOCl]\left(1 + \frac{K}{[H^+]}\right)$$

$$[Cy^{3-}] = \frac{TOTCl - [HOCl]\left(1+\frac{K}{[H^+]}\right)}{3\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + 2\frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2\frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}} \quad (13)$$

Step 2 – Solution of TOTCy in terms of Cy^{3-} (Eq. 14)

$$TOTCy = \frac{[H^+]^3[HOCl]^3[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + \frac{[H^+]^3[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl][Cy^{3-}]}{K_{12}K_{11a}} + \frac{[H^+]^3[Cy^{3-}]}{K_{12}K_{10}K_6} + \frac{[H^+]^2[Cy^{3-}]}{K_{12}K_{10}} + \frac{[H^+][Cy^{3-}]}{K_{12}} + [Cy^{3-}]$$

$$TOTCy = [Cy^{3-}]\left(\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]^3}{K_{12}K_{10}K_6} + \frac{[H^+]^2}{K_{12}K_{10}} + \frac{[H^+]}{K_{12}} + 1\right)$$

$$[Cy^{3-}] = \frac{TOTCy}{\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]^3}{K_{12}K_{10}K_6} + \frac{[H^+]^2}{K_{12}K_{10}} + \frac{[H^+]}{K_{12}} + 1} \quad (14)$$

Step 3 – Solution of working equation (Eq. 15) by setting Eq. 13 equal to Eq. 14

$$\frac{TOTCl - [HOCl]\left(1+\frac{K}{[H^+]}\right)}{3\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + 2\frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2\frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}} = \frac{TOTCy}{\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]^3}{K_{12}K_{10}K_6} + \frac{[H^+]^2}{K_{12}K_{10}} + \frac{[H^+]}{K_{12}} + 1}$$

$$TOTCl - [HOCl]\left(1 + \frac{K}{[H^+]}\right) = TOTCy\frac{3\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + 2\frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2\frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}}{\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]^3}{K_{12}K_{10}K_6} + \frac{[H^+]^2}{K_{12}K_{10}} + \frac{[H^+]}{K_{12}} + 1}$$

$$TOTCl = TOTCy\frac{3\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + 2\frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2\frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}}{\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]^3}{K_{12}K_{10}K_6} + \frac{[H^+]^2}{K_{12}K_{10}} + \frac{[H^+]}{K_{12}} + 1} + [HOCl]\left(1 + \frac{K}{[H^+]}\right)$$

$$0 = TOTCy\frac{3\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + 2\frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2\frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}}{\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]^3}{K_{12}K_{10}K_6} + \frac{[H^+]^2}{K_{12}K_{10}} + \frac{[H^+]}{K_{12}} + 1} + [HOCl]\left(1 + \frac{K}{[H^+]}\right) - TOTCl \quad (15)$$

Figure 7 Derivation of working equation (Eq 15) to solve water chemistry

References

APHA, AWWA & WEF, 2005 (21st ed.). *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association : American Water Works Association : Water Environment Federation, Washington, D.C.

Briggle, T.V., Allen, L.M., Duncan, R.C. & Pfaffenberger, C.D., 1981. High Performance Liquid Chromatographic Determination of Cyanuric Acid in Human Urine and Pool Water. *Journal of the Association of Official Analytical Chemists*, 64:5:1222.

Downes, C.J., Mitchell, J.W., Viotto, E.S. & Eggers, N.J., 1984. Determination of Cyanuric Acid Levels in Swimming Pool Waters by UV Absorbance, HPLC and Melamine Cyanurate Precipitation. *Water Research*, 18:3:277.

HACH Company, 2014a. *Method 8021, Chlorine, Free. USEPA DPD Method, 0.02 to 2.00 mg/L Cl_2*. Hach Company, Loveland, Colorado.

HACH Company, 2014b. *Method 8139, Cyanuric Acid. Turbidimetric Method, 5 to 50 mg/L (Spectrophotometers), 7 to 55 mg/L (Colorimeters)*. HACH Company, Loveland, Colorado.

Hou, S.J. & Ding, M.Y., 2011. Determination of Cyanuric Acid in Milk Powder and Swimming Pool Water by Ion-Pair Reversed-Phase Liquid Chromatography. *Chinese Journal of Chemistry*, 29:4:783.

Kappi, F.A., Tsogas, G.Z., Giokas, D.L., Christodouleas, D.C. & Vlessidis, A.G., 2014. Colorimetric and Visual Read-out Determination of Cyanuric Acid Exploiting the Interaction between Melamine and Silver Nanoparticles. *Microchimica Acta*, 181:5-6:623.

Morris, J.C., 1966. The Acid Ionization Constant of HOCl from 5 to 35c. *The Journal of Physical Chemistry*, 70:12:3798.

O'Brien, J.E., 1972. Hydrolytic and Ionization Equilibria of Chlorinated Isocyanurate in Water. Dissertation. Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts.

O'Brien, J.E., Morris, J.C. & Butler, J.N., 1974. Equilibria in Aqueous Solutions of Chlorinated Isocyanurate. *Chemistry of Water Supply, Treatment, and Distribution*. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Struys, J. & Wolfs, P.M., 1987. Determination of Cyanuric Acid in Swimming Pool Water by Differential Pulse Polarography. *Analytica Chimica Acta*, 199:173.

Sun, H.W., Qin, X.L., Ge, X.S. & Wang, L.X., 2011. Effective Separation and Sensitive Determination of Cyanuric Acid, Melamine and Cyromazine in Environmental Water by Reversed Phase High-Performance Liquid Chromatography. *Environmental Technology*, 32:3:317.

Wajon, J.E. & Carrell Morris, J., 1980. The Analysis of Free Chlorine in the Presence of Nitrogenous Organic Compounds. *Environment International*, 3:1:41.

Whittle, G.P., 1970. Recent Advances in Determining Free Chlorine. *National Specialty Conference on Disinfection*.