

## SUPPORTING INFORMATION

### Mechanism and Kinetics of Cyanogen Chloride Formation from the Chlorination of Glycine

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#### *Estimation of Membrane Diffusivity and Calibration Parameters*

The process separating CNCl from aqueous solution was modeled as pervaporation ( $I$ ) with the tubular membrane being a hollow rod (Figure A-1) (2):

$$\frac{1}{D_m} \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \quad (\text{A-1})$$

$$\text{Boundary Conditions: } C(r = r_i, t) = \alpha C_a(t) \quad (\text{A-2})$$

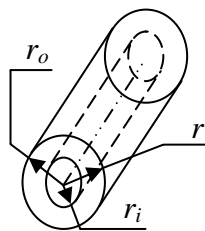
$$C(r = r_o, t) = 0 \quad (\text{A-3})$$

$$\text{Initial Condition: } C(r, t \leq t_d) = 0 \quad (\text{A-4})$$

where  $C$  = CNCl concentration in the membrane,  $\alpha$  = partitioning coefficient between aqueous solution and the membrane,  $D_m$  = diffusion coefficient in the membrane,  $r$  = radius from the center of tubular membrane with  $r_i$  and  $r_o$  being inner and outer radii,  $t$  = reaction time,  $C_a$  = bulk concentration in aqueous solution, and  $t_d$  = time needed to pump reaction solution from the reactor to the membrane. The number of molecules measured in each time interval,  $\tau$ , during which the mass spectrometer conducts a measurement is:

$$I(t) = 2\pi r_o l \varphi \tau D_m \left. \frac{\partial C}{\partial r} \right|_{r=r_o} \quad (\text{A-5})$$

with  $l$  = length of tubular membrane and  $\varphi$  = mass spectrometer multiplier current gain.



**Figure A-1.** Schematic diagram of the membrane introduction tubing.

An analytic solution of Equations (A-1) – (A-4) is available (3) for the case of a constant solution concentration,  $C_a$ , such as when the MIMS is applied to analyze a standard solution, as follows:

$$C(r,t) = \alpha C_a \left[ \frac{\ln(r_o/r)}{\ln(r_o/r_i)} + \pi \sum_{n=1}^{\infty} \frac{J_0(r_i \omega_n) J_0(r_o \omega_n) U_0(r \omega_n) e^{-D_m \omega_n^2 (t-t_d)}}{J_0^2(r_i \omega_n) - J_0^2(r_o \omega_n)} \right] \quad (\text{A-6})$$

where  $n = 1, 2, 3, \dots$  (practically,  $n = 5$  was used in calculation),  $J_0$  = Bessel function of the first kind of zeroth order,  $U_0(r \omega_n) = J_0(r \omega_n) Y_0(r_o \omega_n) - J_0(r_o \omega_n) Y_0(r \omega_n)$  with  $Y_0$  = Bessel function of the second kind of zeroth order,  $\omega_n$  = the roots of  $U_0(r_i \omega_n) = 0$ . Combining Equations (A-5) and (A-6) gives the observed MIMS signal intensity:

$$I(t) = \frac{2\pi l \phi \tau D_m \alpha C_a}{\ln(r_o/r_i)} \left[ 1 - r_o \ln(r_o/r_i) \pi \sum_{n=1}^{\infty} \frac{J_0(r_i \omega_n) J_0(r_o \omega_n) \frac{dU_0}{dr}(r_o \omega_n) e^{-D_m \omega_n^2 (t-t_d)}}{J_0^2(r_i \omega_n) - J_0^2(r_o \omega_n)} \right] \quad (\text{A-7}).$$

As  $t \rightarrow \infty$ , steady state is attained in which

$$I \rightarrow I_{ss} = \frac{2\pi l \phi \tau D_m \alpha C_a}{\ln(r_o/r_i)} = \frac{C_a}{\sigma} \quad (\text{A-8}).$$

The calibration parameter,  $\sigma = \frac{\ln(r_o/r_i)}{2\pi l \phi \tau D_m \alpha}$ , was readily estimated by measuring the steady-state

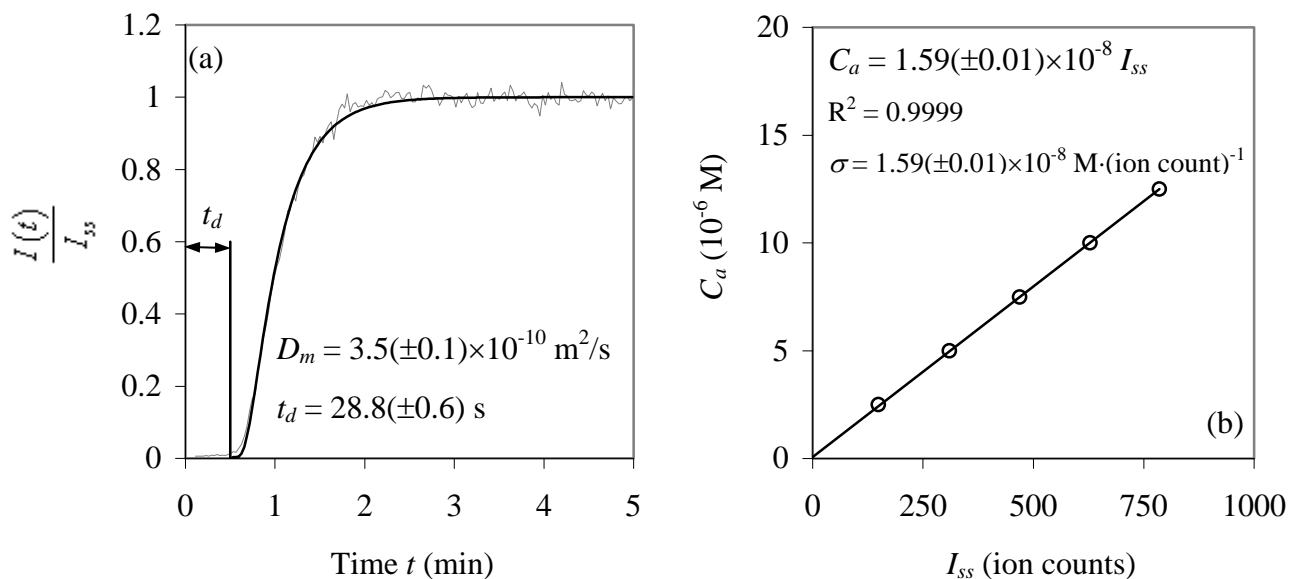
intensity of a set of calibration solutions with known  $C_a$ 's. Normalizing  $I$  by  $I_{ss}$  gives:

$$\frac{I(t)}{I_{ss}} = 1 - r_o \ln(r_o/r_i) \pi \sum_{n=1}^{\infty} \frac{J_0(r_i \omega_n) J_0(r_o \omega_n) \frac{dU_0}{dr}(r_o \omega_n) e^{-D_m \omega_n^2 (t-t_d)}}{J_0^2(r_i \omega_n) - J_0^2(r_o \omega_n)} \quad (\text{A-9}).$$

Fitting Equation (A-9) to the experimental data of  $\frac{I(t)}{I_{ss}}$  vs.  $t$  provided estimates of  $D_m$  and  $t_d$ .

An example obtained with cyanogen chloride standards at pH 7.0 and 25°C is shown in Figure A-2. In Figure A-2(a), the regression using Equation (A-9) provided the estimates of  $D_m = 3.5(\pm 0.1) \times 10^{-10}$  m<sup>2</sup>/s and  $t_d = 28.8(\pm 0.6)$  s. (The values in parentheses here and throughout the Supporting Information are standard deviations.) In Figure A-2(b), the steady-state MIMS observation  $I_{ss}$  and CNCl aqueous concentration  $C_a$  were fitted to a linear relation as depicted by Equation (A-8). The slope of the linear

regression was estimated as  $\sigma = 1.59(\pm 0.01) \times 10^{-8} \text{ M} \cdot (\text{ion count})^{-1}$ . The estimates of  $D_m$ ,  $t_d$ , and  $\sigma$  were shown to be independent of from pH 4 to 8 and from 15 to 35°C (4).



**Figure A-2.** (a) Estimation of  $D_m$  and  $t_d$ . The experiment, conducted with 10  $\mu\text{M}$  CNCl standard at pH 7.0 and 25°C, is represented in gray. The black line is the non-linear fit with Equation (A-9). (b) Calibration curve of cyanogen chloride according to Equation (A-8) at pH 6.99( $\pm 0.02$ ) and 25°C.

### Mass Transfer Corrections in Kinetic Experiments

When  $C_a(t)$  varies, as it does over the course of a reaction, Equations (A-1) – (A-5) must be solved numerically. Solving this set of equations requires the estimates of  $D_m$ ,  $\alpha$ ,  $t_d$ ,  $r_o$ ,  $r_i$ ,  $\varphi$ , and  $\tau$ . Besides  $D_m$  and  $t_d$  estimated above and  $r_o$  and  $r_i$  known from the specifications of the membrane tubing, the estimates of other parameters could not be readily attained. To avoid the estimation of  $\alpha$ ,  $\varphi$ , and  $\tau$ , Equations (A-1) – (A-5) were transformed utilizing the calibration coefficient  $\sigma$ .

Define a new membrane concentration variable  $C'(r,t)$ :

$$C'(r,t) = \frac{C(r,t)}{\alpha\sigma} \quad (\text{A-10}).$$

Rearranging Equation (A-10) with  $\sigma = \frac{\ln(r_o/r_i)}{2\pi l \phi \tau D_m \alpha}$  gives:

$$C(r,t) = \frac{\alpha \ln(r_o/r_i)}{2\pi l \phi \tau D_m} C'(r,t) \quad (\text{A-11}).$$

Replacing  $C(r,t)$  with  $C'(r,t)$  using Equation (A-11), Equations (A-1) – (A-5) become:

$$\frac{1}{D_m} \frac{\partial C'}{\partial t} = \frac{\partial^2 C'}{\partial r^2} + \frac{1}{r} \frac{\partial C'}{\partial r} \quad (\text{A-12})$$

$$\text{B.C.s: } C'(r=r_i, t) = \frac{C_a(t)}{\sigma} \quad (\text{A-13})$$

$$C'(r=r_o, t) = 0 \quad (\text{A-14})$$

$$\text{I.C.: } C'(r, t \leq t_d) = 0 \quad (\text{A-15})$$

$$\text{and } I(t) = -r_o \ln(r_o/r_i) \left. \frac{\partial C'}{\partial r} \right|_{r=r_o} \quad (\text{A-16}).$$

These are Equations (1) – (5) in the main text. With an initial guess of  $C_a(t)$ ,  $I(t)$  was calculated by solving Equations (A-12) to (A-16) using Matlab 6.5 (student release). The calculated profile,  $I'(t)$ , was compared with the experimental intensity measurements and the difference between  $I'(t)$  and  $I(t)$  was used to adjust  $C_a(t)$ .  $I'(t)$  was recalculated and the process was re-iterated until the difference between  $I'(t)$  and  $I(t)$  became negligible. Upon minimizing the difference, an estimate of the aqueous concentration  $C_a(t)$  was obtained. The final  $n$ th estimate,  $C_a(t)_n$ , was assumed to equal to the actual reactor  $C_a(t)$ . The initial guess for  $C_a(t)$  was obtained from  $C_a(t) = \sigma I(t)$ .

The numerical computation of  $C_a(t)$  described above would require an impractically long computation time if the large raw MIMS data sets,  $I(t)$ , were used directly since each data point would have to be transformed separately. To expedite the transformation, it was determined that without loss of precision,  $I(t)$  could first be represented by a polynomial function  $I_{fit}(t)$ , in which the polynomial coefficients were fit with a non-linear regression routine using the Gauss-Newton algorithm with Levenberg-Marquardt modifications. Polynomial functions of the 7<sup>th</sup> degree were found to fit the raw MIMS intensity data well.

In summary, the approach to estimating  $C_a(t)$ , from the experimental measurement  $I(t)$ , involved the following steps:

- (a) Fit the raw MIMS data  $I(t)$  to a 7<sup>th</sup>-degree polynomial  $I_{fit}(t)$ .
- (b) Establish an initial guess for  $C_a(t)$  as  $C_a(t)_{guess} = \sigma I_{fit}(t)$ .
- (c) Numerically solve Equations (A-12) – (A-15) (see Matlab code below) using  $C_a(t)_{guess}$  together with  $D_m$  and  $t_d$  estimated above. A prediction for  $I_{fit}(t)$ ,  $I_{fit}'(t)$ , was calculated based on Equation (A-16).
- (d) A Matlab nonlinear regression routine was applied to iteratively adjust the polynomial coefficients of  $C_a(t)_{guess}$  and minimize the difference between  $I_{fit}(t)$  and  $I_{fit}'(t)$ . One hundred and nineteen points were taken from  $I_{fit}(t)$  and  $I_{fit}'(t)$  (one point every 0.25 minutes starting from  $t = 0.5$  min) to calculate the sum squared error (SSE). The final result  $C_a(t)$  was obtained by minimizing SSE.

The robustness of the entire procedure was assessed in terms of the fraction of variance explained by the modeling,  $R^2$ , for steps (a) and (d) as well as the effects of varying  $C_a(t)_{guess}$ ,  $D_m$ , and  $t_d$  on the resulting  $C_a(t)$  (see the section entitled ‘Robustness of  $C_a(t)$  Estimation Procedure’ below).

#### Matlab Code of $C_a(t)$ Acquisition

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```
function [Iprime,beta] = nlinMIMS(t,I,beta0)
% Iprime = Ifit'(t)
% beta = polynomial coefficients of resulting Ca(t)
% t = reaction time
% I = Ifit(t)
% beta0 = polynomial coefficient of Ifit(t) as Ca(t)guess

[beta r J] = nlinfit(t,I,'MIMSobs',beta0)
% Nonlinear regression routine to acquire Ca(t) by minimizing the difference between Ifit'(t) and
% Ifit(t)
% r = residuals
% J = the Jacobian
% MIMSobs = function that solves the mass transfer model

Iprime = MIMSobs(beta, t)
% Calculate I'fit(t) based on the estimated Ca(t).

function Iprime = MIMSobs(beta0,t)
```

```

% Function to solve for I'fit(t) with Ca(t)guess
% tMIMS = time of MIMS measurements

ri = 0.32
ro = 0.595
% ri and ro = inner and outer radii of membrane introduction tubing.

Dm = 3.82/1000000
td = 0.51
% Dm = diffusivity in the membrane, mm^2/s
% td = time to pump reaction solution from reactor to MI probe, min
% Dm and td must be adjusted for different pH and temperature!!!

tMIMS = t-td
% tMIMS = time of MIMS measurements

x = linspace(ri,ro,10)
% Set radial meshes.

m = 1;
% Setup PDE in cylindrical coordinates.

sol = pdepe(m,@pdex1pde,@pdex1ic,@pdex1bc,x,tMIMS,[],Dm,ri,beta0,td);
% Solve the PDE.

u = sol(:,:,1);
% Extract the first solution component as u.

for j = 2:length(t)
[dummy,I(j)] = pdeval(m,x,u(j,:),ro);
end
% Calculate the gradient at ro.

Iprime = (-I*ro*log(ro/ri))'
% Calculate the flux at ro.

function [c,f,s] = pdex1pde(x,t,u,DuDx,Dmm,ri,beta0,td)
c = 1/Dmm;
f = DuDx;
s = 0;
% PDE setup

function u0 = pdex1ic(x,Dmm,ri,beta0,td)
if x > ri
u0 = 0;
else
u0 = polyval(beta0,td)
end
% Initial Conditions

function [pl,ql,pr,qr] = pdex1bc(xl,ul,xr,ur,t,Dmm,ri,beta0,td)

```

```

pl = ul-polyval(beta0,t+td)
ql = 0;
pr = ur;
qr = 0;
% Boundary Conditions

```

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### *Robustness of $C_a(t)$ Estimation Procedures*

The robustness of  $C_a(t)$  estimation procedures described above were evaluated by the following statistical and sensitivity analyses.

#### *Goodness of Fit of Continuous Function Models of Raw Data*

To assess whether a 7<sup>th</sup>-degree polynomial is a good representation of the experimental data (step (a) above), the fraction of total variation explained by the polynomial model was calculated according to the following equation:

$$R^2 = \frac{\sum [I_{fit}(t) - \bar{I}(t)]^2}{\sum [I(t) - \bar{I}(t)]^2} \quad (\text{A-17})$$

where  $\bar{I}(t) = \frac{\sum I(t)}{n}$  with the number of data  $n = 969$ . For the data shown in Figure 1 in the main text,  $R^2 = 0.997$ . This suggests that 99.7% of the variation about the mean of the MIMS observations can be explained by the polynomial  $I_{fit}(t)$ , and thus the model provides a close fit.

#### *Goodness of $C_a(t)$ Solution to Mass Transfer Model Prediction of $I(t)$*

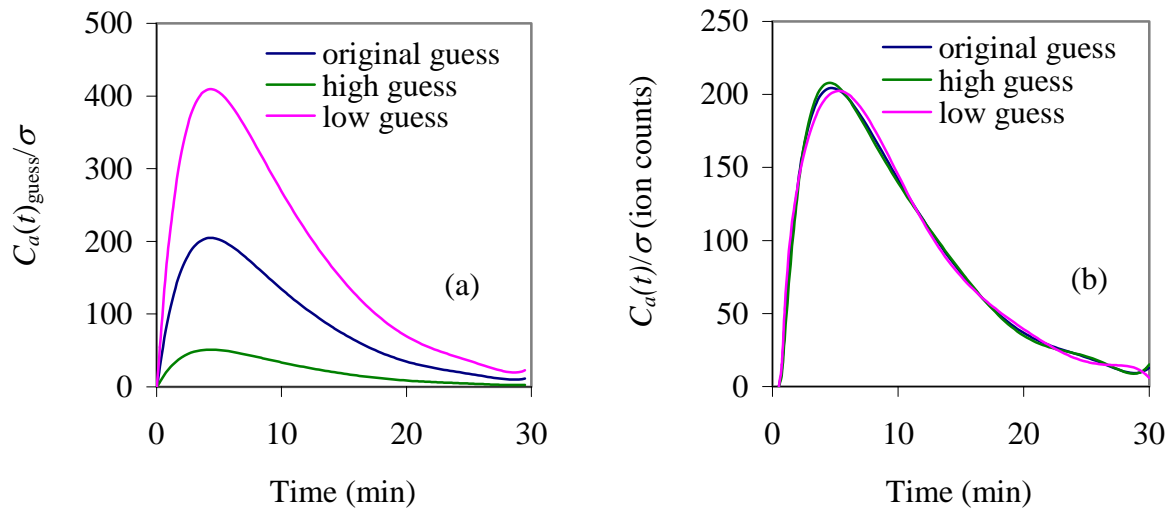
To characterize whether the predicted  $I_{fit}'(t)$ , which corresponds to the final  $C_a(t)_{guess}$ , is a good representation of  $I_{fit}(t)$  (step (d) above), the following correlation coefficient was obtained:

$$R^2 = \frac{\sum [I_{fit}'(t) - \bar{I}_{fit}'(t)]^2}{\sum [I_{fit}(t) - \bar{I}_{fit}(t)]^2} \quad (\text{A-18})$$

where  $\bar{I}_{fit}(t) = \frac{\sum I_{fit}(t)}{n}$  with the number of data  $n = 119$ . For the data shown in Figure 1 in the main text,  $R^2$  was calculated as 0.999 and thus  $I_{fit}'(t)$  was a good representation of  $I_{fit}(t)$ .

### *Effects of Initial Guess on Resulting $C_a(t)$*

The robustness of the numerical solution to Equations (A-12) – (A-15) for  $C_a(t)$  depends in part on whether the solution is independent of the initial guess for  $C_a(t)$ . Original initial guesses for  $C_a(t)$  values were obtained by using the fitted polynomial function for the raw data,  $I(t)$ , i.e.,  $C_a(t)_{guess} = \sigma I_{fit}(t)$  (step (b) above). Two extreme initial guess cases were then tested to determine the independence of the solution to the initial guess. The two cases were designed by either multiplying or dividing the polynomial coefficients in the original  $I_{fit}(t)$  function by 4, respectively. Time profiles of the original guess and two extreme guess cases are plotted as  $C_a(t)_{guess}/\sigma$  in Figure A-3(a). The labels ‘high guess’ and ‘low guess’ cases in this plot correspond to the functions obtained with largest and smallest polynomial coefficient sets. The numerical solution results with all three guess profiles were found to yield essentially the same solution for  $C_a(t)$ , as shown in Figure A-3(b).



**Figure A-3.** (a) The original and two extreme initial guesses used to solve for  $C_a(t)/\sigma$ . (b)  $C_a(t)/\sigma$  obtained with the guesses in (a). This is the same example as shown in Figure 1 in the main text.



### Effects of $D_m$ and $t_d$ on Resulting $C_a(t)$

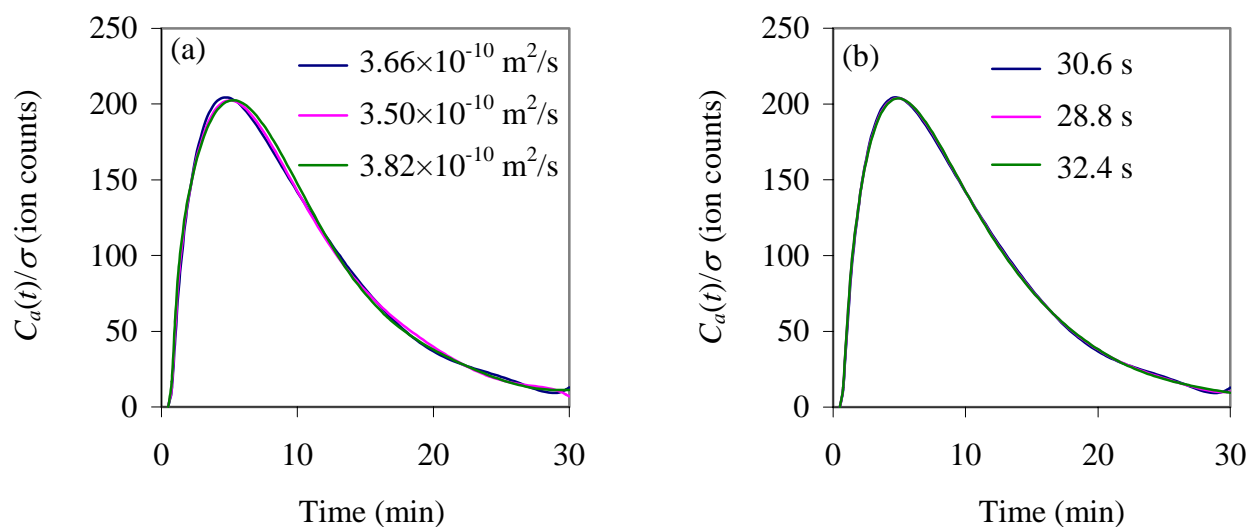
The sensitivity of the  $C_a(t)$  estimates to two other parameters, the diffusion coefficient in the MIMS membrane,  $D_m$ , and the initial time needed to pump reaction solution from the reactor to the membrane,  $t_d$ , was also investigated.

Around pH 7, the two parameters were estimated using CNCl standards (one example is shown in Figure A-2(a)) as:

$$D_m = 3.66(\pm 0.16) \times 10^{-10} \text{ m}^2/\text{s} \quad (\text{A-19})$$

$$t_d = 30.6(\pm 0.6) \text{ s} \quad (\text{A-20})$$

For the experiment shown in Figure 1 in the main text, estimates of  $C_a(t)$  were obtained using upper and lower limit values of  $D_m$  and  $t_d$ . The upper and lower limit values were based on the values in (A-19) and (A-20) plus or minus 3 times their standard deviations, respectively. These ranges for  $D_m$  and  $t_d$  should ideally cover 99% of their possible variation, provided they have a normal distribution. Analyses similar to those used to assess the sensitivity of  $C_a(t)$  to  $C_a(t)_{guess}$ , were used to evaluate the sensitivity of  $C_a(t)$  to variations in  $D_m$  and  $t_d$ , as shown in Figure A-4. These comparisons demonstrate that estimates of  $C_a(t)$  were not sensitive to changes in the parameters over their expected variation ranges.



**Figure A-4.** (a)  $C_a(t)/\sigma$  obtained with  $D_m = 3.66(\pm 0.16) \times 10^{-10} \text{ m}^2/\text{s}$ . (b)  $C_a(t)/\sigma$  obtained with  $t_d = 30.6(\pm 0.6) \text{ s}$ . This is the same example as shown in Figure 1 of the main text.

*Derivation of Equations (20) and (22) in Main Text*

1. Derive expression for  $[\text{CNCl}]_f$  as a function of time,  $t$ .
- a. Derive expression for total  $N,N$ -dichloroglycine concentration as a function of  $t$ .

Since at pH 4 – 8

$$[\text{Cl}_2\text{-Gly}]_T = [\text{NCl}_2\text{CH}_2\text{COOH}] + [\text{NCl}_2\text{CH}_2\text{COO}^-] \quad (\text{B-1})$$

the rate of change of total  $N,N$ -dichloroglycine concentration is due to the first-order decay of  $\text{NCl}_2\text{CH}_2\text{COOH}$  and  $\text{NCl}_2\text{CH}_2\text{COO}^-$ :

$$\frac{d[\text{Cl}_2\text{-Gly}]_T}{dt} = -k_1[\text{NCl}_2\text{CH}_2\text{COOH}] - k_2[\text{NCl}_2\text{CH}_2\text{COO}^-] \quad (\text{B-2}).$$

The concentrations of the two  $N,N$ -dichloroglycine species are related by the following acid dissociation equilibrium:

$$\frac{[\text{NCl}_2\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{NCl}_2\text{CH}_2\text{COOH}]} = K_{a2} \quad (\text{B-3}).$$

Together with the mass balance Equation (B-1), the above equation gives:

$$[\text{NCl}_2\text{CH}_2\text{COO}^-] = \frac{K_{a2}[\text{Cl}_2\text{-Gly}]_T}{K_{a2} + [\text{H}^+]} \quad (\text{B-4})$$

$$\text{and } [\text{NCl}_2\text{CH}_2\text{COOH}] = \frac{[\text{H}^+][\text{Cl}_2\text{-Gly}]_T}{K_{a2} + [\text{H}^+]} \quad (\text{B-5}).$$

Substitution of Equations (B-4) and (B-5) into Equation (B-2) gives:

$$\frac{d[\text{Cl}_2\text{-Gly}]_T}{dt} = -\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]} [\text{Cl}_2\text{-Gly}]_T \quad (\text{B-6}).$$

At any given pH, integrating the above equation gives:

$$[\text{Cl}_2\text{-Gly}]_T = [\text{Cl}_2\text{-Gly}]_{T,o} \exp\left(-\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]} t\right) \quad (\text{B-7})$$

where  $[\text{Cl}_2\text{-Gly}]_{T,o}$  is the initial concentration of total *N,N*-dichloroglycine. Therefore,

$$[\text{NCl}_2\text{CH}_2\text{COO}^-] = \frac{K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{K_{a2} + [\text{H}^+]} \exp\left(-\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]} t\right) \quad (\text{B-8})$$

b. Derive expression for the proposed intermediate concentration,  $[X]$ , as a function of  $t$ .

Since

$$\frac{d[X]}{dt} = k_2 [\text{NCl}_2\text{CH}_2\text{COO}^-] - k_2^* [X] \quad (\text{B-9})$$

Substitution of Equation (B-8) into the above equation gives:

$$\frac{d[X]}{dt} = \frac{k_2 K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{K_{a2} + [\text{H}^+]} \exp\left(-\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]} t\right) - k_2^* [X] \quad (\text{B-10}).$$

Integrating the above equation gives:

$$[X] = \frac{k_2 K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{k_2 K_{a2} + k_1 [\text{H}^+] - k_2^* (K_{a2} + [\text{H}^+])} \left[ \exp(-k_2^* t) - \exp\left(-\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]} t\right) \right] \quad (\text{B-11}).$$

c. Derive expression for  $[\text{CNCl}]_f$  as function of  $t$ .

By the proposed mechanism (see Reactions (17) and (18) of the main text):

$$\frac{d[\text{CNCl}]_f}{dt} = k_2 [X] \quad (\text{B-12})$$

Substitution of Equation (B-11) in the above equation gives:

$$\frac{d[\text{CNCl}]_f}{dt} = \frac{k_2 k_2^* K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{k_2 K_{a2} + k_1 [\text{H}^+] - k_2^* (K_{a2} + [\text{H}^+])} \left[ \exp(-k_2^* t) - \exp\left(-\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]} t\right) \right] \quad (\text{B-13})$$

Integrating the above equation gives:

$$[\text{CNCl}]_f = \frac{k_2 k_2^* K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{k_2 K_{a2} + k_1 [\text{H}^+] - k_2^* (K_{a2} + [\text{H}^+])} \left[ \frac{1 - \exp(-k_2^* t)}{k_2^*} - \frac{1 - \exp\left(-\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]} t\right)}{\frac{k_2 K_{a2} + k_1 [\text{H}^+]}{K_{a2} + [\text{H}^+]}} \right] \quad (\text{B-14}).$$

Define

$$k_{obs} = \frac{k_1 [\text{H}^+] + k_2 K_{a2}}{[\text{H}^+] + K_{a2}} \quad (\text{B-15}).$$

as in Equation (16) of the main text, and applying this definition in Equation (B-14) gives:

$$[\text{CNCl}]_f = \frac{k_2 k_2^* K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{(k_{obs} - k_2^*) (K_{a2} + [\text{H}^+])} \left[ \frac{1 - \exp(-k_2^* t)}{k_2^*} - \frac{1 - \exp(-k_{obs} t)}{k_{obs}} \right] \quad (\text{B-16}).$$

- Derive expressions for  $\theta$  (i.e., Equation (22) of the main text) and final form of  $\frac{[\text{CNCl}]_f}{[\text{CNCl}]_{f,max}}$  as a

function of  $t$  (i.e., Equation (20) in the main text).

When  $t \rightarrow \infty$ , Equation (B-16) becomes:

$$\begin{aligned} [\text{CNCl}]_{f,max} &= \frac{k_2 k_2^* K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{(k_{obs} - k_2^*) (K_{a2} + [\text{H}^+])} \left[ \frac{1-0}{k_2^*} - \frac{1-0}{k_{obs}} \right] \\ &= \frac{k_2 k_2^* K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{(k_{obs} - k_2^*) (K_{a2} + [\text{H}^+])} \left[ \frac{k_{obs} - k_2^*}{k_2^* k_{obs}} \right] \\ &= \frac{k_2 K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{k_{obs} (K_{a2} + [\text{H}^+])} \quad (\text{B-17}). \end{aligned}$$

Applying Equations (10) and (11) of the main text,  $\theta = \frac{[\text{CNCl}]_{f,max}}{[\text{Gly}]_o}$  and  $[\text{Gly}]_o = [\text{Cl}_2\text{-Gly}]_{T,o}$ , and

using Equation (B-17),

$$\theta = \frac{[\text{CNCl}]_{f,max}}{[\text{Cl}_2\text{-Gly}]_{T,o}} = \frac{\frac{k_2 K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{k_{obs} (K_{a2} + [\text{H}^+])}}{[\text{Cl}_2\text{-Gly}]_{T,o}} = \frac{k_2 K_{a2}}{k_{obs} (K_{a2} + [\text{H}^+])} \quad (\text{B-18}).$$

Substituting Equation (B-15) into Equation (B-18) gives:

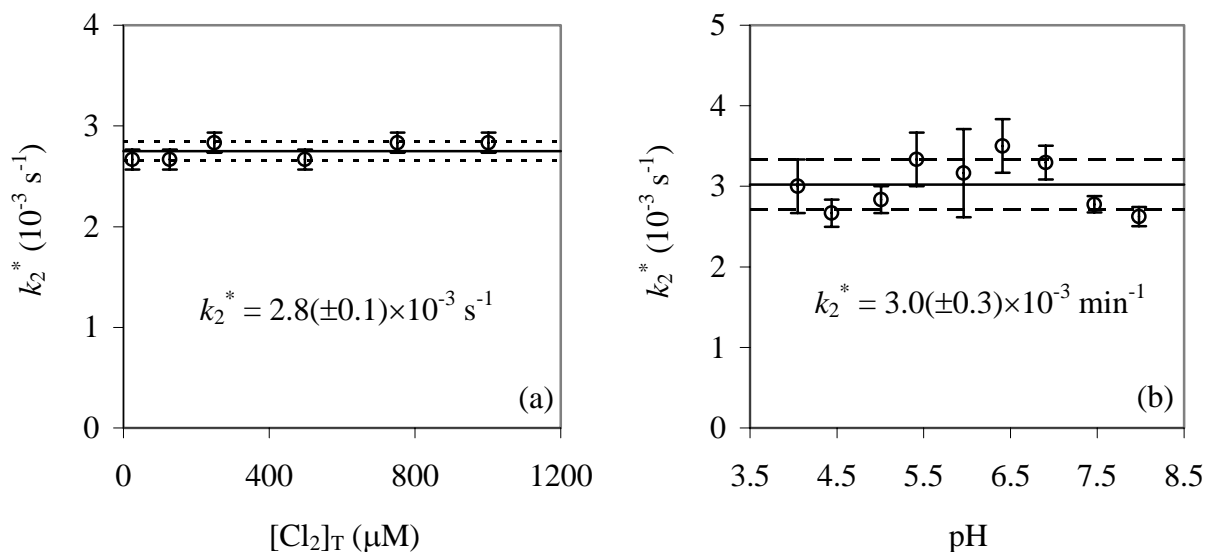
$$\theta = \frac{k_2 K_{a2}}{k_1 [\text{H}^+] + k_2 K_{a2}} \quad (\text{B-19}).$$

This is equation (22) in the main text. The final expression of  $[\text{CNCl}]_f$  as a function of  $t$ , as given by Equation (20) in the main text, can also be derived directly by substituting the results from

Equations (B-16) and (B-17) into the left hand side of Equation (20), i.e.,  $\frac{[\text{CNCl}]_f}{[\text{CNCl}]_{f,max}}$ :

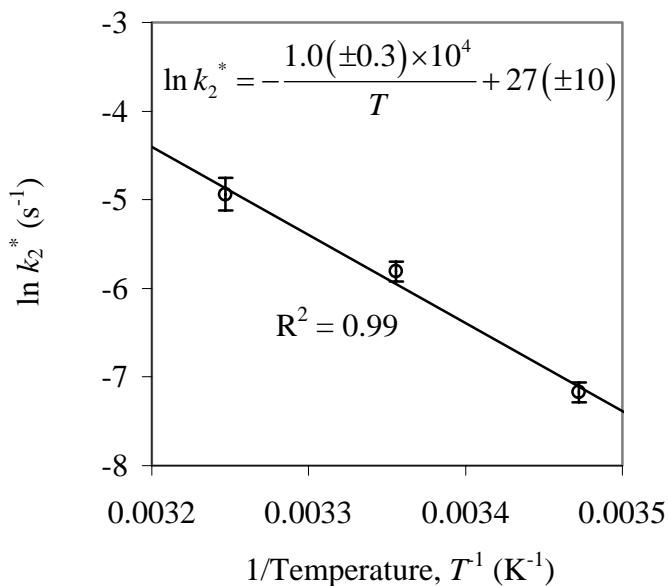
$$\begin{aligned} \frac{[\text{CNCl}]_f}{[\text{CNCl}]_{f,max}} &= \frac{\frac{k_2 k_2^* K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{(k_{obs} - k_2^*) (K_{a2} + [\text{H}^+])} \left[ \frac{1 - \exp(-k_2^* t)}{k_2^*} - \frac{1 - \exp(-k_{obs} t)}{k_{obs}} \right]}{\frac{k_2 K_{a2} [\text{Cl}_2\text{-Gly}]_{T,o}}{k_{obs} (K_{a2} + [\text{H}^+])}} \\ &= \frac{1}{k_2^{*-1} - k_{obs}^{-1}} \left[ \frac{1 - \exp(-k_2^* t)}{k_2^*} - \frac{1 - \exp(-k_{obs} t)}{k_{obs}} \right] \quad (\text{B - 20}). \end{aligned}$$

Dependence of  $k_2^*$  on Free Chlorine Concentration and pH



**Figure C-1.** (a) Dependence of  $k_2^*$  on free chlorine concentration at pH  $5.01(\pm 0.04)$ . (b) Dependence of  $k_2^*$  on pH at  $25^\circ\text{C}$ .

Dependence of  $k_2^*$  on Temperature



**Figure C-2.** Temperature dependence of  $k_2^*$  in the form of a linearized Arrhenius equation.

## Notations

$\alpha$	partition coefficient between aqueous solution and the membrane, unitless.
$\tau$	time interval between MIMS measurements, seconds [s].
$\sigma$	$\frac{\ln(r_o / r_i)}{2\pi l \varphi \tau D_m \alpha}$ , calibration coefficient, micro molar per ion count [M·(ion count) <sup>-1</sup> ].
$\sigma^*$	Taft constant, unitless.
$\varphi$	mass spectrometer multiplier current gain, unitless.
$\omega_n$	the roots of $U_0(r_i \omega_n) = 0$ , unitless.
$[\text{Cl}_2]_{\text{T}}$	concentration of total free chlorine, molar [M].
$[\text{Cl}_2\text{-Gly}]_{\text{T}}$	concentration of total <i>N,N</i> -dichloroglycine, molar [M].
$[\text{Cl}_2\text{-Gly}]_{\text{T},o}$	initial concentration of total <i>N,N</i> -dichloroglycine, molar [M].
$[\text{CNCl}]_d$	hypothetical concentration of CNCl that decayed by OCl <sup>-</sup> -catalyzed hydrolysis, molar [M].
$[\text{CNCl}]_f$	‘cumulative’ concentration of cyanogen chloride formed, molar [M].
$[\text{CNCl}]_{f,max}$	maximum value of $[\text{CNCl}]_f$ , molar [M].
$[\text{Gly}]$	glycine concentration, molar [M].
$[\text{Gly}]_o$	initial glycine concentration, molar [M].
$[\text{H}^+]$	proton concentration, molar [M].
$[\text{NCl=CHCOO}^-]$	concentration of <i>N</i> -chloromethylimine, molar [M].
$[\text{NCl}_2\text{CH}_2\text{COOH}]$	concentration of neutral <i>N,N</i> -dichloroglycine, molar [M].

$[\text{NCl}_2\text{CH}_2\text{COO}^-]$	concentration of carboxylate <i>N,N</i> -dichloroglycine, molar [M].
$[\text{OCl}^-]$	concentration of hypochlorite, molar [M].
$C$	concentration in MIMS membrane, molar [M].
$C_a$	concentration in aqueous solution, molar [M].
$C_a(t)$	time profile of aqueous concentration, molar [M].
$C_a(t)_{\text{guess}}$	initial guess of $C_a(t)$ , molar [M].
$C_a(t)_n$	<i>n</i> th estimate of $C_a(t)$ , molar [M].
$C'$	$\frac{C}{\alpha\sigma}$ , normalized concentration in MIMS membrane, ion counts [ion counts].
$\text{CH}_2=\text{NCl}$	<i>N</i> -chloromethylimine.
$\text{CNCl}$	cyanogen chloride.
$D_m$	diffusion coefficient in MIMS membrane, meters squared per second [ $\text{m}^2/\text{s}$ ].
$\text{Gly}$	glycine.
$I$	ion abundance on the MIMS side, ion counts [ion counts].
$I_{\text{CNCl}}$	ion abundance of $\text{CNCl}$ on the MIMS side, ion counts [ion counts].
$I_{\text{CH}_2=\text{NCl}}$	ion abundance of $\text{CH}_2=\text{NCl}$ on the MIMS side, ion counts [ion counts].
$I_{\text{CH}_2=\text{NCl}, o}$	$I_{\text{CH}_2=\text{NCl}}$ extrapolated to time zero, ion counts [ion counts].
$I_{ss}$	$I$ when $t \rightarrow \infty$ , ion counts [ion counts].
$I(t)$	raw data of MIMS measurements, ion counts [ion counts].



$I(t)$	MIMS intensity time profile calculated based on $C_a(t)$ , ion counts [ion counts].
$I_{fit}(t)$	7 <sup>th</sup> -degree polynomial fit of $I(t)$ , ion counts [ion counts].
$I_{fit}'(t)$	7 <sup>th</sup> -degree polynomial representing MIMS intensity time profile calculated based on $C_a(t)_{guess}$ or $C_a(t)$ , ion counts [ion counts].
$J_0$	Bessel function of the first kind of zeroth order, unitless.
$k_1$	first order rate constant for neutral $N,N$ -dichloroglycine decay, per second [ $s^{-1}$ ].
$k_1^*$	first order rate constant for $N$ -chloromethylimine decay, per second [ $s^{-1}$ ].
$k_2$	first order rate constant for anionic $N,N$ -dichloroglycine decay, per second [ $s^{-1}$ ].
$k_2^*$	first order rate constant for $N$ -chloroiminocarboxylate decay, per second [ $s^{-1}$ ].
$k_{obs}$	pseudo first order rate constant, per second [ $s^{-1}$ ].
$k_{OCl}$	second order rate constant for CNCl decay due to hypochlorite-catalyzed hydrolysis, per molar per second [ $M^{-1}s^{-1}$ ].
$K_{a1}$	ionization constant of anionic $N,N$ -dichloroglycine, molar [M].
$K_{a2}$	ionization constant of neutral $N,N$ -dichloroglycine, molar [M].
$l$	length of tubular MIMS membrane, meters [m].
$n$	integer, unitless.
$r$	radius from the center of tubular MIMS membrane, meters [m].
$r_i$	inner radius of tubular MIMS membrane, meters [m].
$r_o$	outer radius of tubular MIMS membrane, meters [m].
$t$	reaction time, seconds [s].

$T$	absolute temperature, Kelvin [K].
$t_d$	time to pump reaction solution from reactor to MIMS membrane, seconds [s].
$U_0$	$J_0 Y_0 - J_0 Y_0$ , unitless.
$X$	primary intermediate of carboxylate $N,N$ -dichloroglycine decay.
$Y_0$	Bessel function of the second kind of zeroth order, unitless.

### References

- (1) Kotiaho, T.; Lauritsen, F. R.; Choudhury, T. K.; Cooks, R. G.; Tsao, G. T. *Anal. Chem.* **1991**, *63*, A875-&.
- (2) Sysoev, A. A.; Ketola, R. A.; Mattila, I.; Tarkiainen, V.; Kotiaho, T. *Int. J. Mass Spectrom.* **2001**, *212*, 205-217.
- (3) Jaeger, J. C. *Journal and Proceedings of Royal Society of New South Wales* **1940**, *74*, 342-352.
- (4) Na, C. *Formation of Cyanogen Chloride from Amino Acids and Its Stability with Free Chlorine and Chloramine* Ph.D. Dissertaton, University of Michigan, **2005**