

Temperature impact on monochloramine, free ammonia, and free chlorine indophenol methods

Thomas E. Waters^a, Matthew T. Alexander^a and David G. Wahman^{b,*}

^a U.S. Environmental Protection Agency, Office of Water, Office of Ground Water and Drinking Water, Standards and Risk Management Division, Technical Support Center, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA

^b U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Solutions and Emergency Response, Water Infrastructure Division, Drinking Water Management Branch, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA

*Corresponding author. E-mail: wahman.david@epa.gov

Abstract

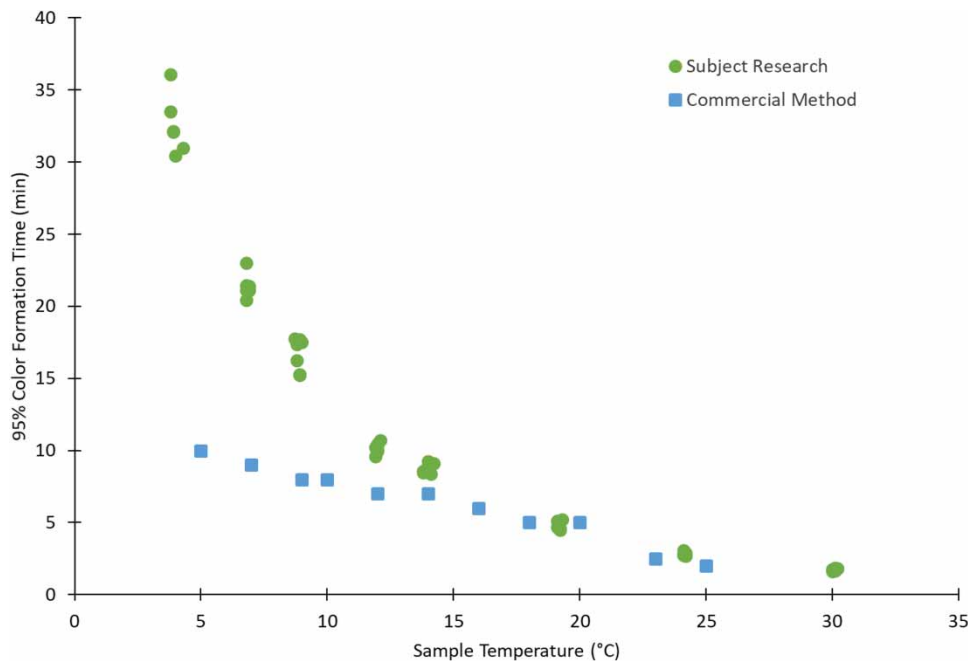
A commercial colorimetric indophenol (IP) method is used for determining monochloramine (NH₂Cl) concentrations for process control in chloraminated public water systems and chloramine-related research. The NH₂Cl – IP method excludes some quality control procedures typically included in drinking water methods and is not approved by the United States Environmental Protection Agency (U.S. EPA) for compliance monitoring. Therefore, the authors developed and validated a more complete NH₂Cl–IP method, building on the commercial technique, as a candidate for future approval. During method development, temperature impact on color development was investigated. Color development time increased as temperature decreased. Below 20 °C, times needed for full color development were greater than those reported in the commercial method, reaching nearly three times longer at 5 °C. This observed temperature dependence also applies to free ammonia and free chlorine indophenol methods. To avoid measurement errors of samples analyzed below 20 °C, use of reaction times determined in this study is recommended for these indophenol methods.

Key words: color development, colorimetry, disinfectant residual, distribution systems, monochloramine, temperature dependence

Highlights

- Temperature dependence of the colorimetric indophenol method was evaluated.
- Reaction times to achieve full color development are up to three times longer than those used in the commercial method that is commonly used to assess drinking water.
- Use of reaction times determined by the authors is recommended to avoid underestimation of monochloramine and free chlorine measurements and variable free ammonia measurements.

Graphical Abstract



INTRODUCTION

In public water systems (PWSs) using chloramines (i.e., combined chlorine) as a disinfectant, monochloramine (NH_2Cl) is the preferred inorganic chloramine species, as compared to dichloramine or trichloramine, because NH_2Cl has a greater (i) taste and odor threshold and (ii) stability (AWWA 2013). Fortunately, NH_2Cl is the dominant inorganic chloramine species formed at typical pH values (i.e., greater than 7) and chlorine-to-ammonia-nitrogen ($\text{Cl}_2:\text{N}$) mass ratios (i.e., less than 5:1) used in PWSs (Jafvert & Valentine 1992; Vikesland *et al.* 2001).

Independent of their regulatory compliance monitoring, PWSs that use chloramines sometimes analyze samples to determine NH_2Cl concentrations with a commercial NH_2Cl indophenol (NH_2Cl – IP) method (Hach Company 2019a). In addition, they sometimes use a free ammonia indophenol (Free NH_3 –IP) method to provide Free NH_3 concentrations that uses the same chemistry as the NH_2Cl – IP method. The measured NH_2Cl and Free NH_3 concentrations may be used to assess (i) effectiveness of process control (e.g., chloramine formation), (ii) maintenance of adequate secondary (i.e., distribution system) disinfectant residual, and (iii) maintenance of conditions in the distribution system to minimize the potential for nitrification (AWWA 2013). Therefore, ensuring accurate NH_2Cl and Free NH_3 concentration measurements are of practical importance to chloraminated PWSs.

The commercial NH_2Cl – IP method is not approved by the United States (U.S.) Environmental Protection Agency (EPA) for compliance monitoring in U.S. PWSs (40 CFR § 141.74 (a)(2)). Thus, those PWSs that (i) need to demonstrate compliance and (ii) wish to use the NH_2Cl – IP method for process control to optimize NH_2Cl residuals and minimize nitrification risk in the distribution system must use multiple methods.

The total chlorine N,N-diethyl-p-phenylenediamine colorimetric (TC-DPD) (APHA AWWA WEF 2017) method is commonly used for compliance monitoring by U.S. PWSs that disinfect with chloramines (AWWA Disinfection Committee 2018), but the TC-DPD method may overestimate disinfection efficacy because of positive interferences from organic chloramines that have no to poor disinfection capability (Donnermair & Blatchley 2003), resulting in an overestimation of the

effective disinfectant concentration (i.e., NH_2Cl). Compared with the TC-DPD method, the NH_2Cl – IP technique has been demonstrated to specifically quantitate NH_2Cl and is not impacted by the presence of dichloramine, trichloramine, or organic chloramines under drinking water conditions (Lee *et al.* 2007). Therefore, the NH_2Cl – IP technique is of interest for assessing the effective disinfectant residuals at PWSs employing chloramine treatment.

At present, Hach Company is the sole provider of powdered reagents for the commercially available NH_2Cl – IP method. Their powder pillow-based method is conducted by (i) adding their powdered reagent (Monochlor F) to a known volume of water sample, (ii) shaking the sample for a specified amount of time to dissolve the reagent, (iii) allowing the sample to develop color for a specified amount of time based on sample temperature, and (iv) analyzing the color development using a portable handheld colorimeter ($\lambda = 610 \text{ nm}$) or benchtop spectrophotometer ($\lambda = 655 \text{ nm}$) to determine the NH_2Cl concentration (Hach Company 2019a). The powdered reagent contains a cyanoferrate that catalyzes a reaction between NH_2Cl present in the sample and a substituted phenol in the powder to form an intermediate monoimine compound (Figure 1). The intermediate monoimine compound couples with excess substituted phenol to form a green-colored indophenol in direct proportion to the concentration of NH_2Cl present in the sample (Hach Company 2019a). This series of reactions (Figure 1) is a modified version of the Berthelot reaction series (Harp *et al.* 2001). To accurately determine the NH_2Cl concentration, it is important that the sample completes color development prior to analysis.

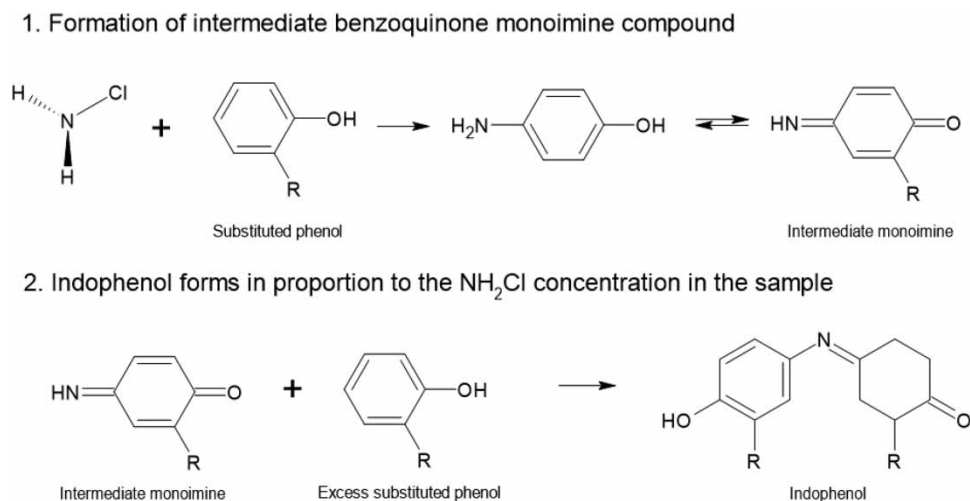


Figure 1 | Schematic of indophenol method reactions.

Towards the goal of ultimately approving a compliance monitoring method to specifically and accurately determine the effective disinfectant concentration in chloraminated PWSs, U.S. EPA's Office of Research and Development (ORD) and Office of Water (OW) undertook development and validation of an EPA NH_2Cl – IP method for determining NH_2Cl concentration, building upon the commercial method. Following multi-laboratory validation and publication, the new method will be a candidate for approval by U.S. EPA as an alternative compliance monitoring method under the Agency's established method-approval process.

During U.S. EPA's NH_2Cl – IP method development, the correlation between sample temperature and rate of color development was investigated and found to deviate from currently published information for the commercial method (Hach Company 2019a, 2019b, 2019c). To provide detailed guidance to water treatment and distribution system operators and state primacy agencies, studies were conducted at a series of water temperatures between 5 and 30 °C.

Although not the focus of the current study, the results presented herein may also apply to the FreeNH₃-IP (Hach Company 2019b) and free chlorine indophenol (FreeCl₂-IP) (Hach Company 2019c) methods because these methods use the same indophenol reaction chemistry. The FreeCl₂-IP method was approved by U.S. EPA for compliance monitoring of FreeCl₂ after it was deemed equally effective relative to the free chlorine DPD compliance monitoring method. In research, temperature is often an experimental variable that is tightly controlled. Therefore, ensuring that adequate time is provided for full color development is important. Consequently, the temperature dependence of reaction times reported in this study has a substantial practical implication to the drinking water community and researchers conducting chloramine-related research. The authors have shared these findings with the developer of the commercial method and are coordinating with them to ensure the use of consistent reaction times. Currently, the commercial method developer has included verbiage in their methods cautioning analysts to re-read samples after 5–10 minutes when sampling in cold weather to ensure full color development. In the future, commercial method manufacturers may reference the reaction times developed in the current research or the future U.S. EPA NH₂Cl-IP method.

MATERIALS AND METHODS

Sample preparation

All solutions were prepared in chlorine demand-free glassware (Summers *et al.* 1996). Prior to use, the glassware was soaked for 24 hours in a 20 mg Cl₂ L⁻¹ sodium hypochlorite (Fisher Chemical, NJ, USA) solution and subsequently rinsed in triplicate with distilled water. A 10,000 mg Cl₂ L⁻¹ FreeCl₂ stock solution was prepared from laboratory-grade sodium hypochlorite and ultra-pure water (UPW, 18.2 MΩ·cm, Milli-Q, Millipore Sigma, MA, USA) and then standardized by spectrophotometry using the known hypochlorite ion (OCl⁻) molar absorptivity (350 cm⁻¹M⁻¹ at 292 nm) (Margerum *et al.* 1994). A 10,000 mg N L⁻¹ FreeNH₃-nitrogen stock solution was prepared from certified ACS-grade ammonium sulfate salt (Fisher Chemical, NJ, USA) in UPW and adjusted to pH 8.3 with sodium hydroxide (NaOH). A 1,000 mg Cl₂ L⁻¹ NH₂Cl stock solution was prepared using the FreeCl₂ and FreeNH₃ stock solutions in UPW with a target Cl₂:N mass ratio of 4:1 and target pH above 8.3 to ensure that NH₂Cl was the predominant chloramine species. The NH₂Cl stock solution was mixed on a magnetic stirrer for 15 minutes to ensure full formation of NH₂Cl from the combination of FreeCl₂ and FreeNH₃ stock solution doses. The NH₂Cl stock solution was then standardized by spectrophotometry using the known NH₂Cl molar absorptivity (445 cm⁻¹M⁻¹ at 245 nm) (Valentine *et al.* 1986). NH₂Cl stock solutions were prepared fresh every 4 hours to minimize NH₂Cl degradation and were standardized by spectrophotometry immediately prior to any use.

NH₂Cl sample solutions for use in the study were prepared from the NH₂Cl stock solution at 2.0 mg Cl₂ L⁻¹ in UPW, buffered with 0.2 mM potassium phosphate monobasic (Fisher Chemical, NJ, USA) and adjusted to pH 9.0 with sodium hydroxide (Fisher Chemical, NJ, USA) to ensure that NH₂Cl was the predominant chloramine species. Experiments were conducted in both high- and low-ionic strength matrices. The high ionic strength (HIS) matrix was prepared by adding 1.40 g of sodium bicarbonate, 1.48 g of sodium sulfate, and 1.54 g of sodium chloride per liter of UPW in addition to the previously described phosphate buffer. The low ionic strength (LIS) matrix was prepared with UPW and the phosphate buffer only.

Experimental approach

The color development times were evaluated in triplicate at 5, 8, 10, 13, 15, 20, 25, and 30 °C in both HIS and LIS water matrices. Aliquots of the 2.0 mg Cl₂ L⁻¹ NH₂Cl solution were transferred

headspace-free into 16 mL amber glass vials. Three individual sample vials were used for each temperature tested. The vials were kept in a circulating water bath at the desired test temperature prior to analysis. The digital temperature display on the water bath was verified with a NIST-traceable thermocouple thermometer (Digi-Sense Traceable Lollipop Thermometer, Cole-Parmer, IL, USA). Prior to each trial, a sample blank was analyzed using the same kinetic program settings and temperature to provide a zero reference for the spectrophotometer. For each temperature tested, a new vial was removed from the water bath, then 6 mL of sample was pipetted to waste, leaving 10 mL of sample in the vial as specified in the commercially available NH_2Cl – IP method (Hach Company 2019a). Pre-packaged, powdered Monochlor F reagent was then added to the vial. The sample was then agitated on a vortexer (Vortex Genie 2, Fisher Scientific, NJ, USA) for 20 seconds to ensure consistent mixing for each sample. The sample was subsequently transferred to a 1 cm quartz cuvette and inserted into a Thermo Scientific Peltier Control and Cooling Unit (Model # PCCU1, Thermo Scientific, MA, USA) fitted in a Thermo Nicolet Evolution UV-Vis 300 spectrophotometer (Thermo Scientific, MA, USA). The rate of color development, as measured by light absorbance at a wavelength of 655 nm, was recorded at 30-second intervals using kinetic software provided with the spectrophotometer. The elapsed time between adding reagent to the 10 mL NH_2Cl sample and beginning the time course analysis in the spectrophotometer was noted and added to the reaction time data (typically 1 minute). The samples were maintained at the target temperatures using the Peltier temperature control unit throughout the kinetic program analysis. The sample temperature was verified with a NIST-traceable thermocouple thermometer prior to and immediately after each set of kinetic temperature measurements to verify that the temperature readout on the Peltier unit was accurate. Depending on the ambient temperature and relative humidity, it was determined that accumulation of condensation on the outside of the cuvette would interfere with absorbance readings, especially at the colder temperatures tested, so the sample compartment on the spectrophotometer was continuously purged with compressed air to prevent condensation from forming on the cuvette during analysis. The spectrophotometer kinetic program was run until full color development, defined as a change in absorbance readings less than 1% relative difference for five consecutive timesteps (i.e., 2.5 minutes).

RESULTS AND DISCUSSION

Reaction time determination

An example color development kinetic curve is shown in Figure 2 (15 °C experiment). The rate of color development follows a sigmoidal pattern, the slope of the linear portion of which is directly proportional to the sample temperature. Greater temperatures had faster color development and correspondingly steeper slopes. Figure 2 is representative of all temperatures tested in that, at a given temperature, little to no difference in the rate of absorbance development or final absorbance value was observed between experimental trials or between the HIS versus LIS matrices at a given temperature, indicating the reproducibility and limited impact of ionic strength on color development rate.

To determine the time required for full color development, 95% of the final absorbance value (as defined in the experimental approach) measured at 655 nm was selected for each experimental trial. This assumes a 5% error in determining reaction completion, which is generally acceptable for this type of method (Vogel *et al.* 1989). For each triplicate temperature trial conducted in both HIS and LIS matrices, the time corresponding to 95% of the final absorbance (t_{95}) was calculated (Figure 3).

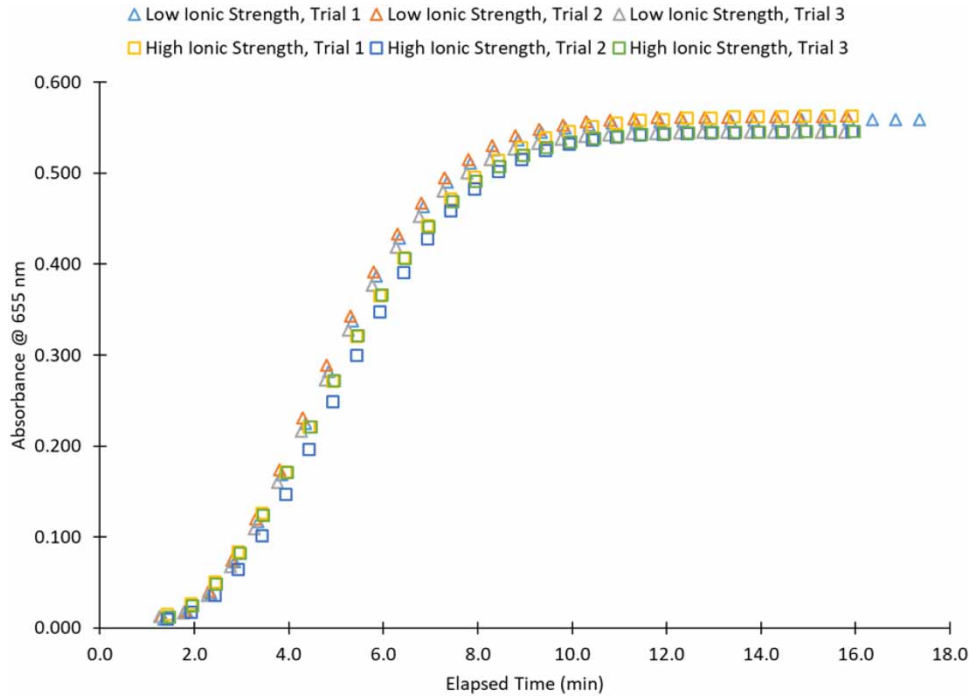


Figure 2 | Color development at 15 °C for the monochloramine indophenol method.

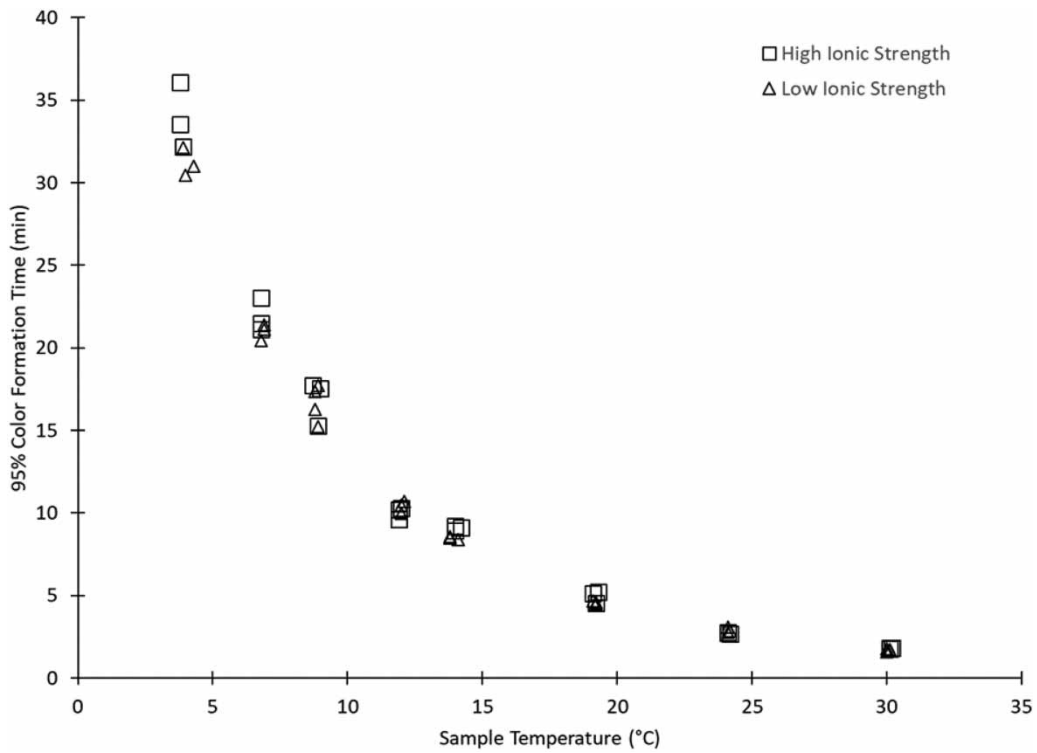


Figure 3 | Temperature impact on 95% color formation time in both high- and low-ionic strength water matrices.

Assuming the reagent is in excess and color formation is proportional to reacted NH_2Cl (i.e., Beer's Law), color formation may be represented as a pseudo-first-order reaction (Equation (1)).

$$1 - F_t = \frac{C_t}{C_0} = e^{-kt} \tag{1}$$

In Equation (1), t is time (minutes); F_t is the fraction of color formation relative to the final absorbance at time t ; C_t is the unreacted NH_2Cl concentration ($\text{mg Cl}_2 \text{ L}^{-1}$) remaining in the sample; and k is the rate constant for the reaction of NH_2Cl with the method reagents (min^{-1}). For any specific F_t (e.g., $F_t = 0.95$, which represents 95% color formation) and using Equation (1), the corresponding time (i.e., t_{95}) is proportional to k (Equation (2)).

$$k = -\frac{\ln 0.05}{t_{95}} = \frac{3.0}{t_{95}} \quad (2)$$

The degree to which k changes with temperature can be described by the Arrhenius equation (Equation (3)), which is an empirical relationship commonly used to represent temperature dependence of the reaction rate constants (i.e., k) (Stumm & Morgan 1996).

$$\ln k = \ln \frac{3.0}{t_{95}} = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad (3)$$

In Equation (3), T is temperature (Kelvin, K), E_a is the activation energy of the reaction ($\text{J}\cdot\text{mol}^{-1}$); R is the ideal gas constant ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), A is a constant, and k and t_{95} are as previously described. Because of the relationship of k to t_{95} from Equation (2), Equation (3) also represents the theoretical impact of temperature on t_{95} . Equation (3) can be rearranged in the form of a linear equation where E_a/R is the slope, $(\ln 3 - \ln A)$ is the intercept, $\ln t_{95}$ is the ordinate, and $1/T$ is the abscissa (Equation (4)).

$$\ln t_{95} = \frac{E_a}{R} \left(\frac{1}{T} \right) + (\ln 3 - \ln A) \quad (4)$$

Equation (4) was regressed using the observed t_{95} versus T data and results are presented in Figure 4. The observed R^2 of 0.99 supports the hypothesis that the reaction between NH_2Cl and the IP method reagents can be modelled as a pseudo-first-order relationship with an Arrhenius temperature dependence.

Table 1 summarizes the upper 95% confidence limit t_{95} values determined from linear regression and compares them to the recommended reaction times reported in the commercial indophenol methods. The color development times determined in the current study are greater than those recommended by the three commercial indophenol methods at temperatures less than 20 °C. They are almost three times as great for 5 °C. The practical implication for water treatment practice is that NH_2Cl concentrations measured following the color development time recommendations associated with the commercial NH_2Cl – IP methods underestimate the actual NH_2Cl concentration (or FreeCl_2 concentration if using the FreeCl_2 –IP methods) for samples with temperatures below 20 °C.

Practical implications on monochloramine and free chlorine measurement

Even though U.S. EPA's research indicates that reaction times presented in the commercial indophenol methods are too short at temperatures less than 20 °C, it should be noted that results obtained using the shorter reaction times would underestimate the actual NH_2Cl or FreeCl_2 concentration. Therefore, NH_2Cl or FreeCl_2 concentration measurements determined using reaction times specified in the existing commercial methods would be conservative with regard to measuring disinfectant residual and thus generally be more protective of public health with regard to maintaining a disinfectant residual.

Accordingly, underestimation of NH_2Cl or FreeCl_2 concentrations may lead to unintended consequences in PWS operation. For instance, operators may unnecessarily implement strategies to

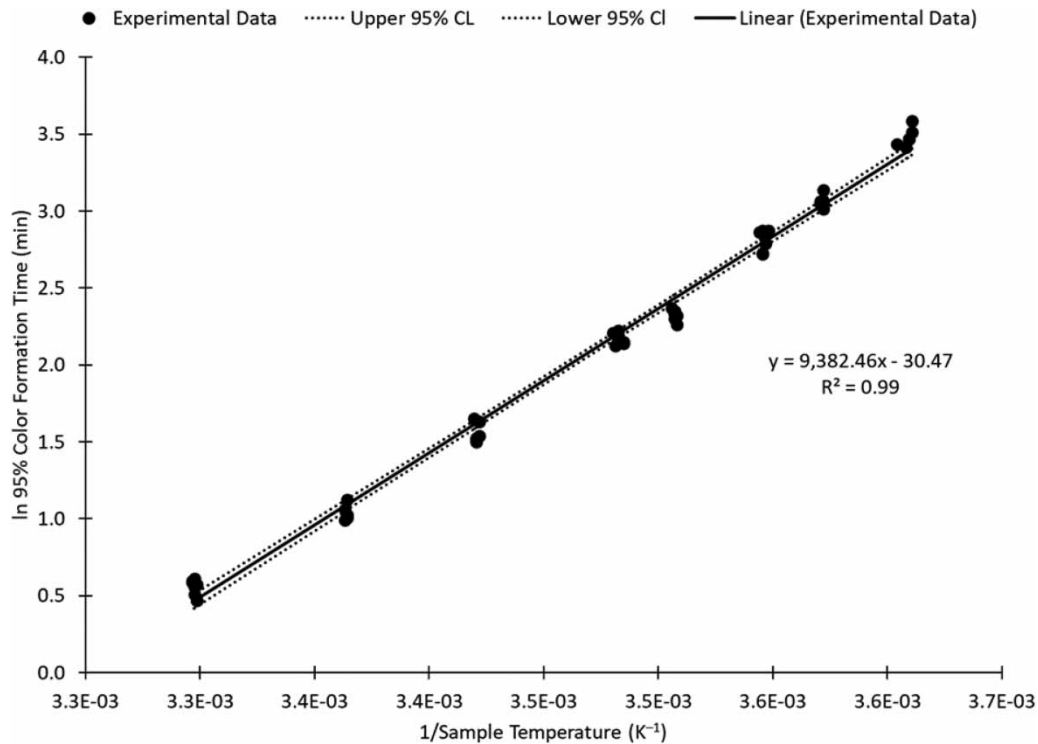


Figure 4 | Arrhenius relationship for 95% color formation time.

Table 1 | Impact of temperature on color development time for indophenol methods

Sample temperature [°C]	Sample temperature [°F]	Current research determined color development time [min]	Commercial method reported color development time [min] ^a
5	41	28	10
7	45	22	9
9	48	17	8
10	50	15	8
12	54	12	7
14	57	10	7
16	61	8	6
18	64	6	5
20	68	5	5
23	73	4	2.5
25	77	3	2
30	86	2	2

^aTimes are the same for the commercial monochloramine, monochloramine and free ammonia, and free chlorine methods (Hach Company 2019a, 2019b, 2019c).

increase the NH_2Cl or FreeCl_2 dose to meet predefined residual targets. The unnecessary increase may result in additional disinfection byproduct formation or potential exceedance of the maximum residual disinfectant level for NH_2Cl or FreeCl_2 of $4.0 \text{ mg Cl}_2 \text{ L}^{-1}$.

When conducting PWS field sampling at ambient temperatures less than 20°C , two factors may lead to water sample temperatures increasing prior to and during measurement. First, sample analysis may occur in a field vehicle, and second, physical handling of samples will tend to increase sample temperature. If the sample temperature increases after the sample temperature is measured to

determine the appropriate reaction time (Table 1), the reaction times reported in the subject study would be conservative (i.e., the time required for complete color development would be less than that specified based on the original sample temperature because the actual temperature at time of analysis is greater). In practice and given the small (10 mL) sample volume used in the method, it is likely that one, or both, of the stated scenarios would occur in cold conditions (e.g., less than 10 °C in the field). Therefore, to avoid potentially long reaction times, analysts should measure sample temperature just prior to sample analysis. Note that this discussion applies to the use of powdered reagents (i.e., Monochlor F) and not the portable parallel analyzer planar cuvette method that is also commercially available from the same vendor (Hach Company 2015, 2016). The commercially available portable parallel analyzer warms the sample, adjusts reaction times for sample temperature, and determines the reaction time automatically.

In contrast to PWS compliance monitoring and process control sampling, chloramine-related laboratory research often controls experimental conditions for temperature, and measurements at temperatures less than 20 °C may be more likely (i.e., in a laboratory environment, samples are less subject to the warming described in the previous paragraph). Therefore, the longer reaction times determined in this study are particularly important to help ensure accurate measurements during laboratory-based research studies.

Practical implications on free ammonia measurement

The current study also has implications for FreeNH₃ measurement by the FreeNH₃–IP method. But, as opposed to the NH₂Cl – IP or FreeCl₂–IP methods, where using an inadequate color development time will bias the NH₂Cl or FreeCl₂ measurement low, providing inadequate times in the FreeNH₃–IP method may bias the FreeNH₃ measurement either low or high.

The FreeNH₃–IP method uses two aliquots from a single sample to determine the FreeNH₃ concentration by difference, and for both aliquots it is important to provide the minimum time for full color development. The first sample aliquot (A1) is prepared as per the NH₂Cl – IP method, where Monochlor F reagent is added and allowed to react for the recommended time. Then A1 is used to blank the spectrophotometer or colorimeter. The second sample aliquot (A2) is used to measure the FreeNH₃ concentration and is treated in two steps. First, FreeNH₃ Chlorinating Reagent (sodium hypochlorite and sodium hydroxide) is added to A2, reacting FreeNH₃ present in A2 into NH₂Cl. Second, and as with A1, Monochlor F reagent is added to A2 and allowed to react for the recommended time. Then A2 is measured on the instrument previously blanked with A1. The increase in color from A1 to A2 is proportional to the sample's FreeNH₃ concentration.

If full color development does not occur in either A1 or A2, the measured FreeNH₃ will be biased, and the bias may be either higher or lower, depending on which aliquot(s) did not reach full color development. To understand the potential practical implications, it is important to also note that after full color development is reached, the developed color is reported stable for at least 15 minutes (Hach Company 2019a, 2019b, 2019c). This 15-minute minimum color stability time was also confirmed through experiments conducted as part of U.S. EPA's NH₂Cl method development and validation. Therefore, it would be logical to assume an analyst may allow A1 or A2 or both to react up to 15 minutes longer than the minimum recommended time as there is no perceived impact.

Based on the previous discussion and the current study, four practical scenarios (Table 2) can be envisioned when sample temperatures are less than 20 °C and the current commercial FreeNH₃–IP method is used. All scenarios assume a theoretical sample is measured at 15 °C and contains NH₂Cl and FreeNH₃ concentrations of 2.0 mg Cl₂ L⁻¹ and 0.25 mg N L⁻¹, respectively. As previously stated, there is no perceived detriment in letting A1 or A2 react longer than the minimum prescribed time. But, if full color development has not occurred when using the commercial method times for samples below 20 °C, then allowing a longer time than the minimum commercial method time will

Table 2 | Implications of inadequate color development times on free ammonia measurement with the commercial free ammonia indophenol method

Scenario	Is full color development reached in sample aliquot before use?		Method measured free ammonia concentration [mg N/L]	Percent of sample free ammonia concentration
	A1	A2		
1	No	No	0.17	68
2	Yes	No	0.06	24
3	No	Yes	0.35	140
4	Yes	Yes	0.24	96

Theoretical sample contains 2 mg Cl₂/L monochloramine and 0.25 mg N/L free ammonia at 15 °C.

A1 = first sample aliquot used as an instrument blank.

A2 = second sample aliquot used to measure free ammonia concentration.

No = indicates using the commercial method minimum recommended color development time of 6 minutes.

Yes = indicates using the subject research minimum recommended color development time of 9 minutes.

impact results as color development will continue in A1 and A2 until reaching full color development. The four scenarios in Table 2 represent combinations of using two color development times at 15 °C (Figure 2): (i) the commercial method time of 6 minutes, meaning that full color development was not reached ($F_t = 0.68$) and (ii) the time of 9 minutes, as determined in the current study, meaning full color development is reached ($F_t = 0.95$) based on acceptable measurement error (Vogel *et al.* 1989).

In Scenarios 1, 2, and 3 (Table 2), A1 and/or A2 use the commercial method's minimum recommended time of 6 minutes. Because at least one aliquot does not reach full color development, resulting measured FreeNH₃ concentrations are biased and range from 24 to 140% of the actual FreeNH₃ concentration. By comparison, using the 9-minute time of the current study for both A1 and A2 (Scenario 4, Table 2) results in a simulated FreeNH₃ measurement that is 96% of the actual FreeNH₃ concentration and within acceptable measurement error (Vogel *et al.* 1989). Overall, the provided example illustrates the potential variability in measured FreeNH₃ concentration when using reaction times that are too short (i.e., Scenarios 1, 2, and 3) for full color development. The practical implications of this example are important for an operator using the commercial FreeNH₃-IP method (below 20 °C) when measuring FreeNH₃ for process control (e.g., chloramine formation or nitrification prevention). The variability in FreeNH₃ measurement could lead to difficulty in meeting target FreeNH₃ concentrations. Therefore, ensuring the minimum color development time is met is necessary to minimize unnecessary uncertainty in FreeNH₃ measurements.

CONCLUSIONS

The temperature study reported herein was part of a larger development and validation study to produce a U.S. EPA NH₂Cl-IP method for measuring NH₂Cl concentrations in drinking water samples. The required reaction times for stable color development in the analyzed samples were determined at a series of temperatures ranging from 5 °C to 30 °C. Color development time increased as sample temperature decreased and could be described by an Arrhenius relationship. The appropriate color development times determined in the subject study were greater (sometimes significantly so) than those described in the three commercially available indophenol methods (NH₂Cl-IP, FreeNH₃-IP, and FreeCl₂-IP) for temperatures less than 20 °C. Overall, to avoid underestimation of NH₂Cl and FreeCl₂ measurements and potentially variable FreeNH₃ measurements in conditions less than 20 °C, it is recommended that reaction times determined in the subject study be used rather than those specified in the commercial NH₂Cl-IP, FreeNH₃-IP, or FreeCl₂-IP methods.

ACKNOWLEDGEMENTS

The authors acknowledge Glynda Smith, Will Adams, and Nick Dugan with the U.S. EPA (Cincinnati, OH, USA) for their assistance and advice in this work, and Scott Tucker (Hach Company, Loveland, CO) for fruitful discussions concerning the indophenol methods. This work has been subjected to the United States Environmental Protection Agency's (Agency's) review and has been approved for publication. The views expressed in this manuscript are those of the authors and do not necessarily represent the views or policies of the Agency. Any mention of trade names, products, or services does not imply an endorsement by the Agency. The Agency does not endorse any commercial products, services, or enterprises.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- APHA, AWWA, WEF 2017 *Standard Methods for the Examination of Water and Wastewater*, 23rd edn. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC.
- AWWA 2013 *Manual of Water Supply Practices M56: Nitrification: Prevention and Control in Drinking Water* (Routt, J. S. J. ed.). American Water Works Association, Denver, CO.
- AWWA Disinfection Committee 2018 *2017 Water Utility Disinfection Survey Report*. AWWA Technical & Educational Council, American Water Works Association, Denver, CO.
- Donnermair, M. M. & Blatchley, E. R. 2003 [Disinfection efficacy of organic chloramines](#). *Water Research* **37**(7), 1557–1570.
- Hach Company 2015 *Method 10269, Ammonia, Free. Indophenol Method, 0.05 to 0.50 mg/L as NH₃-N, Chemkey Reagents*. Loveland, Colorado.
- Hach Company 2016 *Method 10270, Chloramine (Mono). Indophenol Method, 0.04 to 4.60 mg/L as Cl₂, Chemkey Reagents*. Loveland, Colorado.
- Hach Company 2019a *Method 10171, Chloramine (Mono). Indophenol Method, 0.04 to 4.50 mg/L Cl₂ (LR), Powder Pillows*. Loveland, Colorado.
- Hach Company 2019b *Method 10200, Chloramine (Mono) and Nitrogen, Free Ammonia. Indophenol Method, 0.04 to 4.50 mg Cl₂/L or 0.01 to 0.50 mg/L NH₃-N*. Loveland, Colorado.
- Hach Company 2019c *Method 10241, Free Chlorine USEPA Indophenol Method, 0.04 to 4.50 mg Cl₂/L*. Loveland, Colorado.
- Harp, D. L., Weise, P. & Franklin, S. 2001 Controlling Chlorination of Wastewater and Chloramination of Drinking Water. US Patent 6,315,950.
- Jafvert, C. T. & Valentine, R. L. 1992 [Reaction scheme for the chlorination of ammoniacal water](#). *Environmental Science & Technology* **26**(3), 577.
- Lee, W., Westerhoff, P., Yang, X. & Shang, C. 2007 [Comparison of colorimetric and membrane introduction mass spectrometry techniques for chloramine analysis](#). *Water Research* **41**, 3097–3102. doi:10.1016/j.watres.2007.04.032.
- Margerum, D. W., Schurter, L. M., Hobson, J. L. & Moore, E. E. 1994 [Water chlorination chemistry: nonmetal redox kinetics of chloramine and nitrite ion](#). *Environmental Science & Technology* **28**(2), 331–337.
- Stumm, W. & Morgan, J. J. 1996 *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd edn. Wiley, Hoboken, New Jersey.
- Summers, R. S., Hooper, S. M., Shukairy, H. M., Solarik, G. & Owen, D. 1996 [Assess DBP yield: uniform formation conditions](#). *Journal of the American Water Works Association* **88**(6), 80–93.
- Valentine, R. L., Brandt, K. I. & Jafvert, C. T. 1986 [A spectrophotometric study of the formation of an unidentified monochloramine decomposition product](#). *Water Research* **20**(8), 1067–1074.
- Vikesland, J. P., Ozekin, K. & Valentine, R. L. 2001 [Monochloramine decay in model and distribution system waters](#). *Water Research* **35**(7), 1766–1776.
- Vogel, A. I., Furniss, B. S., Hannaford, A. J., Smith, P. W. G. & Tatchell, A. R. 1989 *Vogel's Textbook of Practical Organic Chemistry*, 5th edn. Longman Scientific & Technical, Essex.