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Comparison of colorimetric and membrane introduction mass spectrometry techniques for chloramine analysis

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ABSTRACT

Three methods for the determination of chloramines in water were compared using pH-buffered nanopure water and natural organic matter (NOM) solutions. We investigated whether the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method and/or an adapted indophenol method (Hach MonochlorF) are suitable for determining the concentration of monochloramine in drinking water. Membrane introduction mass spectrometry (MIMS) was used as a reference analysis method to determine the different chloramine species in water. All methods measured monochloramine accurately in Nanopure water, but the DPD colorimetric method measured higher residuals (inorganic and organic chloramines) than MonochlorF or MIMS when in the presence of NOM due to organic chloramines. The indophenol method (MonochlorF) accurately detected only monochloramine and not other chloramine forms. Overall, the monochloramine concentration measured by MonochlorF was comparable with the MIMS results. A combined chlorine residual approach by the DPD colorimetric method does not differentiate between monochloramine and organic chloramines. Therefore, DPD colorimetric methods can overestimate disinfection efficacy in chloraminated water systems because of interference from organic chloramines that have no or poor bactericidal ability. Compared with the DPD colorimetric method, MonochlorF is a better choice for chloraminated water systems.

1. Introduction

The United States has introduced more stringent regulations regarding the formation of some disinfection by-products because of public health concerns. As a result, water treatment plants are reducing their use of free chlorine disinfection and increasing chloramine use. A 2005 survey of 363 community water systems in the US reported that 29% of the utilities currently use chloramines for secondary disinfection in water distribution systems, and another 3% are in the process of converting to chloramines (Seidel et al., 2005).

Chloramination of water produces inorganic mono- (NH_2Cl), di- ($NHCl_2$) and/or tri- (NCl_3) chloramines depending on pH; in the presence of organic nitrogen, organic chloramines also form (Morris, 1967; Ginwalla and Miklta, 1992; Westerhoff et al., 2006). In a companion study, drinking water averaged 0.2 mg/L of organic nitrogen (Lee et al., 2006). Organic nitrogen-containing materials form organic chloramines by reacting with free chlorine ($HOCl/OCl^-$) or inorganic chloramines (NH_2Cl, $NHCl_2$) (Shang et al., 2000; Yang and Shang, 2004). Because organic chloramines have no or poor bactericidal ability relative to inorganic chloramines, their presence can lead to an overestimation of actual disinfection

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capabilities (Feng, 1966; Wolfe et al., 1985; Donnermair and Blatchley III, 2003). While organic chloramine formation in wastewater has been studied (Choshen et al., 1990; Conyers et al., 1993; Scully et al., 1996; Bedner et al., 2004), less information is available on organic chloramines in drinking water systems.

The chloramine detection method most commonly accepted by state agencies for water treatment plants and distribution systems is calculating combined chlorine, the residual chlorine existing in chemical combination with ammonia or organic amines (i.e., inorganic and organic chloramines), by the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method. Combined chlorine quantification involves subtracting free chlorine concentration (by DPD free reagents) from the total chlorine concentration (by DPD total reagents). Many organic as well as inorganic chloramines produce color for DPD total techniques (Wolfe et al., 1985; Derrigan et al., 1993; APHA et al., 1998), thus yielding misleading measurements of desired disinfectant (monochloramine) concentration (Conyers et al., 1993; Scully et al., 1996).

Based on DPD colorimetric methods, other researchers have postulated reactions between inorganic chloramines and organic matter, and have estimated rate constants for such reactions (Vikesland et al., 1998). These and other studies may not have accurately measured monochloramine, however, if the natural organic matter (NOM) contained appreciable levels of organic nitrogen. Monochloramine (NH_2Cl), the dominant inorganic chloramine species at typical water treatment conditions (pH 7–9), needs to be differentiated from combined chlorine residual (inorganic and organic chloramines) to quantify the true disinfection efficacy of chloramination. Membrane introduction mass spectrometry (MIMS) has proven a fast and reliable technique to quantify inorganic chloramines alone (Shang and Blatchley, 1999). However, operating this laboratory instrument requires a high level of expertise.

The objective of this study was to examine whether the DPD colorimetric method and/or an adapted indophenol method (MonochlorF, Hach Co., USA) are suitable for determining the concentration of monochloramine in chloraminated drinking water systems. MIMS was used to quantitatively measure inorganic chloramine species to validate results from the colorimetric techniques. We demonstrated that MonochlorF accurately detects only monochloramine and not other chloramine forms. Using colorimetric and MIMS methods, we showed how organic chloramines can lead to an overestimation of true disinfection efficacy when using DPD reagents.

2. Materials and methods

2.1. *Free chlorine and inorganic chloramines standards*

Free chlorine standard solutions were prepared by diluting sodium hypochlorite solution with phosphate buffer (pH 7). The solution was standardized before use by a titrimetric method, Standard Method 4500-Cl F (APHA et al., 1998). Dilution to target concentrations was accomplished with nanopure water (NANOpure Infinity, IA, USA). Standard inorganic chloramine solutions were prepared daily as described in the literature (Shang and Blatchley, 1999). A monochloramine standard solution was prepared at pH 8.3, and dichloramine and trichloramine standard solutions were prepared at pH 5.0. The concentrations of the inorganic chloramine solutions were titrimetrically standardized prior to each experiment.

2.2. *Experimental approach*

Experiments were performed in nanopure water and NOM solutions buffered with phosphate (pH 5.5 and 7.5; 2 mM) or borate (pH 9.5; 2 mM). Each experiment was conducted in triplicate. The NOM solution was prepared by dissolving a hydrophobic acid NOM isolate obtained from Lake Pleasant (Arizona, USA) water (Mash et al., 2004) in deionized and buffered water. The NOM isolate had a carbon to nitrogen ratio of 30 mg-C/mg-N. The NOM solution (dissolved organic carbon (DOC) = 10 mg/L of C) was dosed with preformed monochloramine at an initial concentration of 1.7 mg/L as Cl_2. After 24 h of reaction in 40-mL amber glass bottles with septa capped at 20 °C in the dark, we measured residuals of total chlorine, free chlorine, and inorganic chloramines (mono-, di-, and tri-chloramine). A separate experiment was conducted with the same NOM (Lake Pleasant) solution and the same monochloramine dose (1.7 mg/L as Cl_2) at pH 7.5 in 1-L completely stirred repipette amber glass containers in triplicate. Samples were taken over 5 days at 2, 6, 12, 24, 48, 72, and 120 h for analysis of total chlorine, free chlorine, and inorganic chloramines.

A further comparison of monochloramine measurements by the MonochlorF and MIMS methods were performed using 16 NOM isolates provided by the University of Poitier, France. Details of the NOM isolation procedures and the characteristics of the NOM isolates are provided elsewhere (Croue et al., 1999; Lee et al., 2006; Westerhoff et al., 2006). Solutions were prepared by dissolving the NOM isolates in nanopure water such that the dissolved organic nitrogen (DON) concentrations were 0.4 mg-N/L; the pH was adjusted to 7.5 with phosphate buffer (2 mM). The DOC to DON ratios of the NOM solutions ranged from 7 to 45 mg-C per mg-N. The solutions were monochloraminated in 40-mL amber glass bottles with septa capped at 20 °C in the dark. The initial monochloramine dosage was 4 mg as Cl_2 per mg DON. Samples were collected from each bottle after 2 and 24 h and subsequently analyzed for total and free chlorine and inorganic chloramines.

2.3. *Analytical methods*

Total and free chlorine were measured by the DPD colorimetric method, Standard Method 4500 Cl G (APHA et al., 1998). After reaction with total and free DPD reagents (Hach Co., USA), light absorbance of samples was measured at 530 nm using a UV/vis spectrophotometer, MultiSpec-1501 (Shimadzu Corp., Japan). Chlorine concentrations were obtained using a standard curve correlating absorbance with standard chlorine concentrations.

Monochloramine was measured using the MonochlorF reagent (Hach Co., USA), which is based on the indophenol