

Evidence that Monochloramine Disinfectant Could Lead to Elevated Pb Levels in Drinking Water

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Many water districts have recently shifted from free chlorine (in the form of HOCl/OCl⁻) to monochloramine (NH₂Cl) as a disinfectant for drinking water to lower the concentration of chlorinated hydrocarbon byproducts in the water. There is concern that the use of NH₂Cl disinfectant may lead to higher Pb levels in drinking water. In this study, the electrochemical quartz crystal microbalance is used to compare the effects of these two disinfectants on the dissolution of Pb films. A 0.5 μm thick Pb film nearly completely dissolves in a NH₂Cl solution, but it is passivated in a HOCl/OCl⁻ solution. X-ray diffraction analysis shows that the NH₂Cl oxidizes Pb to Pb(II) species such as Pb₃(OH)₂(CO₃)₂, whereas the stronger oxidant, HOCl/OCl⁻, oxidizes Pb to Pb(IV) as an insoluble PbO₂ conversion coating. Although NH₂Cl may produce less halogenated organic byproducts than HOCl/OCl⁻ when used as a disinfectant, it may lead to increased Pb levels in drinking water.

Introduction

Free chlorine has traditionally been used as a disinfectant in drinking water because of its ability to inactivate most pathogenic microorganisms quickly (1). However, chlorine reacts with organic compounds present in the water to produce halogenated organic byproducts such as trihalomethanes (THMs), which are suspected to be carcinogens (2). In 1998, the U.S. Environmental Protection Agency (EPA) established a maximum contaminant limit of 80 ppb for total trihalomethanes in drinking water (3). In an attempt to meet this low level of trihalomethanes, several water utilities have switched from free chlorine (in the form of HOCl/OCl⁻) to chloramines such as monochloramine (NH₂Cl) because of their weaker tendency to produce halogenated organic byproducts. Coincident with the shift from free chlorine to NH₂Cl have been reports by some water districts of Pb levels in drinking water that exceed the action limit of 15 ppb set by the EPA. Lead levels of up to 48 000 ppb were observed in Washington, DC, in the fall of 2003, following their shift from free chlorine to NH₂Cl in the 2000 (4, 5). Elevated Pb levels were also reported in Greenville, NC, drinking water after the switch from free chlorine to NH₂Cl was made (6). The monochloramine may lead to high Pb levels by oxidizing Pb in service lines, solder, and brass to soluble Pb(II) (5, 7). Edwards and Dudi (5) have shown that monochloramine

can lead to increased rates of leaching of Pb from Pb-containing brass fixtures. Schock and co-workers (8) have suggested that free chlorine is a sufficiently powerful oxidant that the Pb is passivated by being oxidized to insoluble PbO₂. They have shown by X-ray diffraction (XRD) that the Pb service lines in Cincinnati, OH, are lined with a layer of PbO₂ (8). Cincinnati has a history of using free chlorine in their disinfectant program.

In this paper, we use the electrochemical quartz crystal microbalance (EQCM) to compare the effects of NH₂Cl and HOCl/OCl⁻ on the dissolution of Pb films. The EQCM can measure nanogram changes in mass on the electrode surface while the electrode is immersed in solution by monitoring the changes in resonant frequency of a quartz oscillator (9). We have previously used the EQCM to follow the electrodeposition of layered Cu/Cu₂O nanostructures in real time (10). The EQCM has been used by other groups to study corrosion processes, including anodic corrosion layers on Pb in sulfuric acid (11, 12). We also examine the Pb films by scanning electron microscopy (SEM) and glancing-angle XRD after exposing them to the two disinfectants.

Experimental Section

Disinfectant Solutions. All experiments were conducted using HPLC-grade water from Aldrich. A sodium hypochlorite solution with 10–13 vol % available chlorine was used as a source for HOCl/OCl⁻. Monochloramine and HOCl/OCl⁻ solutions were prepared fresh for each experiment. The NH₂Cl solutions were prepared by reacting OCl⁻ with a 5-fold molar excess of aqueous NH₃ (13, 14). The excess NH₃ minimizes the formation of dichloramine (NHCl₂). To prepare the NH₂Cl solutions, 5 mL of 100 mM NH₃ was added to a rapidly stirred 20 mL solution of 5 mM NaOCl. The pH was adjusted to 8 with 10 mM H₂SO₄; 1 mL of 100 mM KCl was added as an external Cl⁻ source, and the solution was diluted to a total volume of 100 mL. The final concentrations in the solution were approximately 1 mM NH₂Cl, 4 mM NH₄⁺, and 1 mM Cl⁻. At pH 8, the unreacted ammonia is predominately NH₄⁺. The relatively high concentrations of disinfectants in this study were used so that the concentration of the disinfectants remained relatively constant during the corrosion studies, and because the concentrations of the 1 mM solutions could be determined spectrophotometrically. The actual concentrations of OCl⁻ and NH₂Cl were determined spectrophotometrically at 292 nm ($\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$) and 243 nm ($\epsilon = 461 \text{ M}^{-1} \text{ cm}^{-1}$), respectively, using molar absorptivities from the literature (13). The spectrophotometric measurements were made with a CARY 5 UV–Vis–NIR spectrophotometer.

Pb Electrodeposition and Dissolution. Films of Pb were electrodeposited with an EG&G model 273A potentiostat/galvanostat. The polycrystalline Pb films were electrodeposited at a constant current density of 15 mA/cm² from a solution of 0.1 M Pb(ClO₄)₂ in 1 M HClO₄. The films were deposited onto Au-coated, commercially available 9 MHz AT-cut quartz crystals (Seiko model QA-AM9-Au) that were used for the EQCM experiments. The Pb films were used immediately after deposition for the EQCM studies. XRD analysis showed that the films were Pb, with no evidence of PbO. The EQCM electrodes were installed in a Teflon holder so that only one electrode face with an area of 0.2 cm² was exposed to the solution. The total mass of Pb deposited was 112 μg. The electrodeposited Pb films were then exposed to separate 35 mL unstirred 1 mM solutions of NH₂Cl and HOCl/OCl⁻. Each solution was adjusted to a pH of 8 and contained

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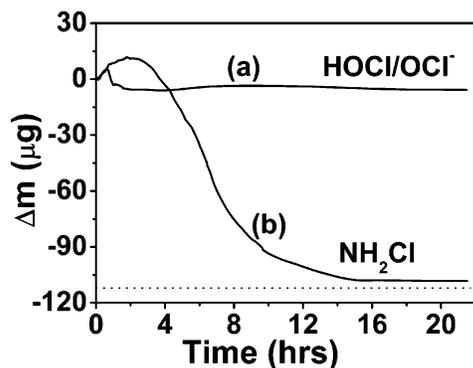


FIGURE 1. EQCM measurement of the change in mass of 0.5 μm thick Pb films immersed in 1 mM solutions of (a) HOCl/OCl⁻ and (b) NH₂Cl at pH 8. The extent of dissolution of Pb is greater in the NH₂Cl solution. The dashed line corresponds to total dissolution of the 112 μg Pb film.

1 mM Cl⁻. No effort was made to exclude dissolved CO₂ from the HOCl/OCl⁻ and NH₂Cl solutions. The mass of Pb was determined as a function of time after treatment with the two disinfectants by monitoring the frequency change of the EQCM electrode using a quartz crystal analyzer (Seiko model QCA917). A gate time of 1 s and an output range of ± 20 kHz/10 V were used with the analyzer. The concentration of Pb in the solutions after the treatment with the two disinfectants was determined by flame atomic absorption spectroscopy using a Varian model SpectrAA 50 atomic absorption spectrometer with a Pb lamp at a wavelength of 217 nm. The detection limit of the instrument is approximately 0.1 ppm. Solutions were not filtered prior to atomic absorption analysis.

XRD and SEM Instrumentation. Grazing incidence X-ray diffraction (XRD) patterns were obtained with a Philips X'Pert diffractometer using Cu K α source radiation with an X-ray mirror (PW3088/60) as the incident beam module and a 0.18° parallel plate collimator as the diffracted beam module. A fixed incident angle of 1° was maintained, and the instrument was operated in the continuous mode with a step size of 0.03° and a counting time of 10 s. SEM micrographs were obtained with a Hitachi model S4700 cold field-emission scanning electron microscope.

Results and Discussion

Figure 1 shows the mass of the Pb electrode as a function of time in the NH₂Cl and HOCl/OCl⁻ solutions. The Pb dissolves to a much greater extent in the NH₂Cl solution than it does in the HOCl/OCl⁻ solution. The decrease in mass of the 112 μg Pb film in HOCl/OCl⁻ is $\sim 5 \mu\text{g}$, while the decrease in mass in the NH₂Cl solution is 107 μg . The Pb film turned red after treatment with HOCl/OCl⁻, and it turned white after treatment with NH₂Cl. The red color after treatment with HOCl/OCl⁻ is consistent with the formation of PbO₂ on the electrode surface. We have shown in unpublished experiments that reddish-brown PbO₂ powder (verified by X-ray diffraction) is formed when HOCl/OCl⁻ is added to a pH 8 aqueous solution of Pb(II). Figure 2 shows SEM micrographs of electrodeposited Pb films after treatment with the two disinfectants. The Pb film is covered with nanometer scale crystallites after the HOCl/OCl⁻ treatment (Figure 2a), while the surface contains platelets after the NH₂Cl treatment (Figure 2b). Glancing-angle XRD analysis of the films shows that the film treated with HOCl/OCl⁻ contains primarily α -PbO₂ and unreacted Pb, with a small amount of β -PbO₂ (Figure 3a). The minor peaks due to β -PbO₂ are marked with an asterisk in Figure 3a. On the basis of the line broadening in the XRD pattern, the crystallite size of the α -PbO₂ is 11

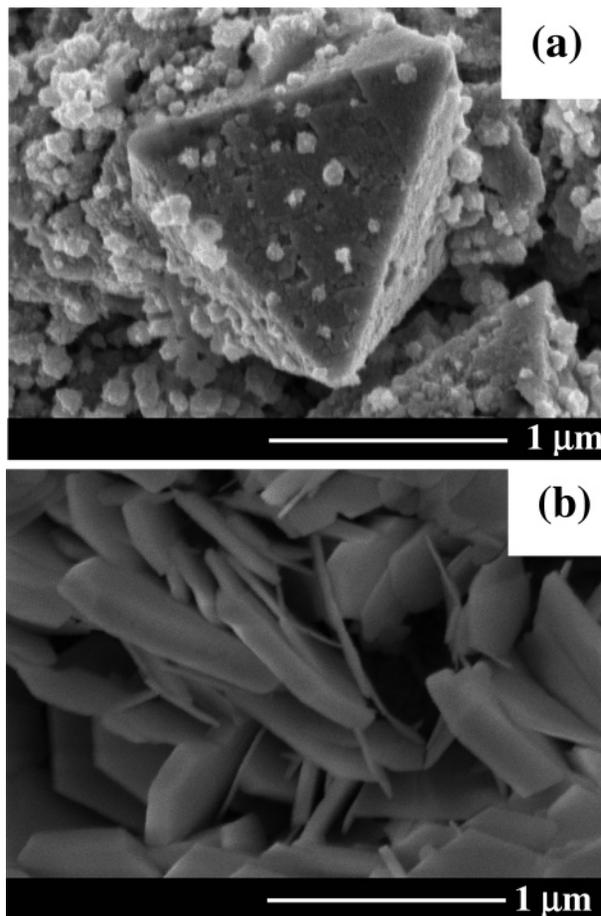


FIGURE 2. Scanning electron micrographs of 0.5 μm thick Pb films immersed in 1 mM solutions of (a) HOCl/OCl⁻ and (b) NH₂Cl at pH 8.

nm. The crystallite size was calculated from the broadening of the (111) reflection of PbO₂ using the Scherrer equation (15). The triangular facets in Figure 2a are [111]-oriented Pb covered with a conversion coating of nanocrystalline PbO₂ produced by the HOCl/OCl⁻ oxidation. The film treated with NH₂Cl contains only divalent Pb in the form of hydrocerussite, Pb₃(OH)₂(CO₃)₂, with no evidence of PbO₂ or unreacted Pb (Figure 3b). The EQCM, SEM, and XRD experiments show that exposing the Pb to NH₂Cl causes the Pb to dissolve and form Pb₃(OH)₂(CO₃)₂. Hydrocerussite is commonly found as a coating on the inside of Pb service lines (16).

After the Pb films were treated with the two disinfectants, the solutions were analyzed for Pb by atomic absorption spectroscopy (AA). The AA analysis showed 0.2 ppm (close to the detection limit of 0.1 ppm) Pb for the solution containing HOCl/OCl⁻ and 1.7 ppm Pb for the NH₂Cl-containing solution. The greater dissolution of Pb in the NH₂Cl solution is consistent with the higher solubility of Pb₃(OH)₂(CO₃)₂ compared with that of PbO₂. The K_{sp} values for Pb₃(OH)₂(CO₃)₂ and PbO₂ are $10^{-18.8}$ and 10^{-66} , respectively (17, 18).

The standard reduction potential of the NH₂Cl/Cl⁻ couple in both acidic and alkaline solutions can be estimated using the equilibrium constant for eq 1 that was determined by Margerum and co-workers from kinetic measurements (19), the standard reduction potentials for HOCl/Cl⁻ and OCl⁻/Cl⁻, and the pK_a for NH₄⁺/NH₃ ($pK_a = 9.25$) (20). The calculated standard reduction potential for NH₂Cl in alkaline solution (eq 2) is 0.69 V versus the normal hydrogen electrode (NHE), and the calculated standard reduction potential for

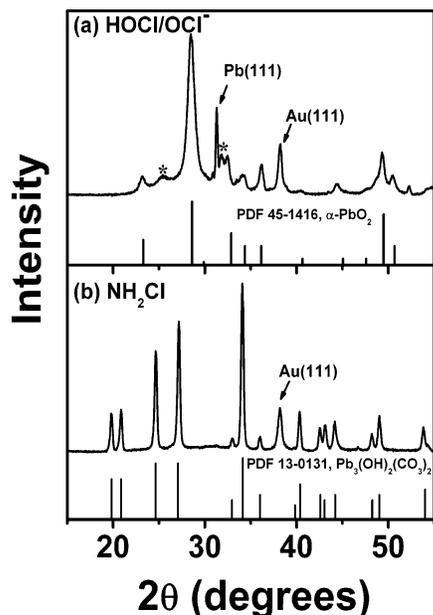
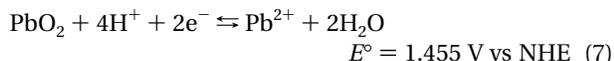
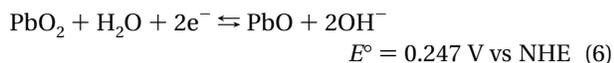
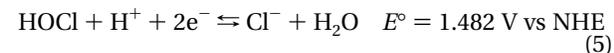
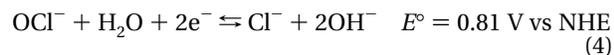
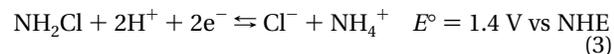
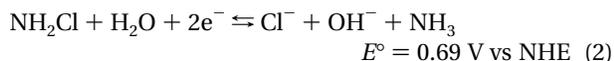


FIGURE 3. Glancing-angle X-ray diffraction patterns of 0.5 μm thick Pb films after immersion in 1 mM solutions of (a) HOCl/OCl⁻ and (b) NH₂Cl at pH 8. The standard powder patterns for α -PbO₂ and Pb₃(OH)₂(CO₃)₂ are shown in panels a and b, respectively. The Pb film exposed to HOCl/OCl⁻ contains primarily α -PbO₂, unreacted Pb, and a small amount of β -PbO₂ (marked with an asterisk). The Pb film exposed to NH₂Cl contains only Pb₃(OH)₂(CO₃)₂, with no remaining Pb. The Au(111) peaks in both diffraction patterns are from the Au-coated EQCM electrode. The X-ray radiation was Cu K α .

NH₂Cl in acidic solution (eq 3) is 1.4 V versus the NHE. The standard reduction potentials for free chlorine and PbO₂ reduction in eqs 4–7 are taken from the literature (20).



Free chlorine (HOCl/OCl⁻) is a slightly stronger oxidizing agent than NH₂Cl in both acidic and alkaline media, consistent with our results. Because the pK_a of HOCl is 7.40 (20), the free chlorine is predominately OCl⁻ at pH 8. At this pH, the solution is 80 mol % OCl⁻ and 20 mol % HOCl. We cannot determine from our experiments whether OCl⁻ or HOCl is the active species in the oxidation reactions.

The standard reduction potentials shown for eqs 2–7 are for all of the reactants and products at unit activity. Formal reduction potentials for these reactions at pH 8 can also be estimated from the Nernst equation for the concentrations used in this study and for Pb²⁺ concentrations at the action

limit of 15 ppb (7.2×10^{-8} M). Formal reduction potentials for the NH₂Cl/Cl⁻, HOCl/Cl⁻, OCl⁻/Cl⁻, and PbO₂/Pb²⁺ couples are 1.0, 1.25, 1.17, and 0.72 V versus the NHE, respectively. Hence, both disinfectants are thermodynamically capable of oxidizing Pb(II) to PbO₂ according to these calculations. The fact that NH₂Cl does not produce a passivating PbO₂ layer suggests either that there is an error in the calculated standard reduction potentials for eqs 2 and 3 due to uncertainty in the equilibrium constant for eq 1 (21, 22) or that the mechanism for oxidation of Pb by NH₂Cl favors the two-electron pathway over the four-electron pathway.

We have performed measurements of the equilibrium potentials of monochloramine and free chlorine at pH 8 by measuring the open-circuit potential of a Pt electrode in solutions of the same concentrations that were used in this study. The potentials were measured versus a saturated calomel electrode (SCE) and then converted to the normal hydrogen electrode by adding 0.242 V. The equilibrium potentials that we measured for monochloramine and free chlorine at pH 8 were 0.65 and 1.02 V versus the NHE, respectively. These measured equilibrium potentials are more consistent with our experimental results than the calculated formal potentials, because they predict that NH₂Cl will oxidize Pb to Pb(II), but it is not a sufficiently powerful oxidant to produce PbO₂. These equilibrium potential measurements suggest that a modern electrochemical study (e.g., rotating disk voltammetry) of the thermodynamics and kinetics of the reduction of both free chlorine and NH₂Cl is warranted.

Free chlorine and monochloramine are not simple outer-sphere electron-transfer agents. Margerum et al. (19) have shown that the oxidation of nitrite ion by NH₂Cl proceeds by acid-catalyzed transfer of Cl⁺ from NH₂Cl to NO₂⁻ to produce NO₂Cl as an intermediate. The mechanism of oxidation of Pb by NH₂Cl is probably more complicated than the simple electron transfer that is suggested in eqs 2 and 3. Our EQCM studies do show, however, that NH₂Cl is capable of dissolving Pb by producing Pb(II). Treatment of the Pb with HOCl/OCl⁻ leads to a lower level of Pb dissolution, due to the production of a conversion coating of PbO₂ on the Pb. Although NH₂Cl may produce less halogenated organic byproducts than free chlorine when used as a disinfectant in drinking water, it may lead to increased Pb levels.

Acknowledgments

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