ES&T RESEARCH

Interferences by Monochloramine and Organic Chloramines in Free Available Chlorine Methods. 1. Amperometric Titration

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■ The free available chlorine (FAC) amperometric titration measurement is subject to interference errors from chloramines. Current measurements from chloramines were as much as 17% of the total chlorine in the presence of a 2:1 molar excess of free amine at 0 V vs SCE. Interferences with this method increased as the positive applied voltage on the platinum electrode decreased. This trend was observed with both model compounds and chlorinated process waters. The interference from combined chlorine in one chlorinated and settled drinking water was up to 50% of the FAC response. Current increases after each addition of phenylarsine oxide (PAO) were observed with *N*-chlorosuccinimide, but not with the other chloramines tested.

Introduction

Chlorine is commonly used in the United States for the disinfection of drinking water, wastewater, and swimming pools. The presence of a free chlorine residual ([HOCl] + [OCl$^-$]) is often regarded as a sign of adequate disinfection. U.S. Environmental Protection Agency regulations (*1*) allow for the replacement of microbiological assays with free available chlorine (FAC) residual measurements in some finished drinking waters. For this reason, accurate free chlorine residual measurements are imperative. Interference in the measurement of free chlorine by poorer disinfectants could result in a false assessment of the microbiological status of treated water.

Monochloramine and organic chloramines are formed by the reaction of chlorine and ammonia or chlorine and nitrogenous organics (*2, 3*). These compounds are poor disinfectants (*4*). Thus, it is important to investigate the ability of these substances to interfere with the analysis of free chlorine.

Two of the most commonly used methods for the analysis of free chlorine are the amperometric titration and *N,N*-diethyl-*p*-phenylenediamine (DPD) procedures. The

an applied voltage of +200 mV. Interferences in the amperometric titration FAC measurement have been observed with several organic chloramines, including the *N*-chloro derivatives of cyanuric acid (*7*) and piperidine (*8*) and the disinfectant halazone [4-(*N,N*-dichlorosulfamyl)benzoic acid] (*9*).

This study reports the response of the amperometric titration method to monochloramine and organic chloramines relative to the response to free chlorine. Relative response factors are examined as a function of applied voltage. Perturbation of the chlorine-free chlorine equilibrium by the titrant is investigated. Model compound results are compared to the analysis of chlorinated field samples.

Experimental Section

Nitrogenous organics and *N,N*-diethyl-*p*-phenylenediamine oxalate (Eastman Kodak Co., Rochester, NY) were used as received. Substrates were buffered at pH 7 with 0.005 M KH_2PO_4 neutralized with NaOH and chlorinated at a 2:1 molar substrate to chlorine ratio. The total chlorine concentration was 5.72×10^{-5} M. Ammonia (NH_4Cl) was chlorinated at a 3:1 molar ammonia to chlorine ratio. Chlorinated mixtures were stored in the dark at 25 °C for approximately 30 min prior to analysis.

Amperometric titrations were performed with a hook-type rotating platinum electrode (rotator S-76485, Pt electrode S-30421; Sargent-Welch Scientific Co., Skokie, IL), saturated calomel reference electrode (SCE), and MP-1000 series voltage source and signal conditioning components (McKee-Pedersen Instruments, Danville, CA). The applied voltage was +200 mV (vs SCE), unless otherwise stated. Current measurements for the current–voltage studies were made with a handheld digital multimeter (Micronta, Tandy Corp., Fort Worth, TX). The phenylarsine oxide titrant (Fisher Scientific Co., Pittsburgh, PA; nominally 0.00564 N) was standardized against