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Electrochemical Determination of Trihalomethanes in Water by Means of Stripping Analysis

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ABSTRACT: A protocol has been developed and evaluated for the determination of trihalomethanes (THMs) at the submicromolar concentration level in water. This method is based on a three-step stripping analysis that utilizes a single electrochemical cell and that entails (a) direct electrochemical reduction of a trihalomethane at a silver cathode to form halide ions in an aqueous sample containing tetraethylammonium benzoate, (b) capture of the released halide ions as a silver halide film on the surface of a silver gauze anode, and (c) cathodic reduction and quantitation of the silver halide film by means of differential pulse voltammetry. Using this procedure, we have determined THMs individually; bromoform and chloroform have been successfully quantitated in 30 min and with a detection limit of 3.0 μg L^{-1} (12 nM) and 6.0 μg L^{-1} (50 nM), respectively. In addition, we have employed our methodology to determine the total trihalomethane (TTHM) content in a prepared water sample at a level commensurate with the maximum allowable annual average of 80 μg L^{-1} mandated by the United States Environmental Protection Agency. We have compared our TTHM results to those obtained by an independent testing laboratory.

(1) $CHX_3 + 3H^+ + 6e^- \xrightarrow{\text{electrolysis}} CH_4 + 3X^-$

(2) $Ag + X^- \xrightarrow{\text{deposition}} AgX(s) + e^-$

(3) $AgX(s) + e^- \xrightarrow{\text{stripping}} Ag + X^-$

Trihalomethanes (THMs) are a group of disinfection byproducts (DBP) including chloroform, bromodichloromethane, dibromochloromethane, and bromoform ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$, respectively) that form when drinking water is chlorinated and the dissolved chlorine gas reacts with natural humic acids and inorganic species in the water. Among these four THMs, chloroform is the most frequently detected volatile organic compound in the groundwater supply of the United States.[1] Trihalomethanes, even at low levels, constitute one of the largest categories of environmental pollutants associated with toxic, mutagenic, carcinogenic, and teratogenic effects on humans.[2−5] In the United States, the Environmental Protection Agency (EPA) has published a document, "Stage 2 Disinfectants and Disinfection By-products Rules," aimed at regulating the total trihalomethane (TTHM) level in drinking water at a maximum allowable annual average of 80 μg L^{-1}; for example, if one is speaking about chloroform, this concentration level is equivalent to 80 ppb or 670 nM.[2,6−8] Thus, the determination of THMs at trace levels has become an important subject in analytical, environmental, and clinical chemistry.

So far, the most prevalent form of measurement has been either liquid chromatography[9] or gas chromatography.[10] Highly selective and sensitive determination of THMs can be achieved by means of these techniques. Purge-and-trap capillary-column gas chromatography interfaced with a mass spectrometer is utilized by the EPA to achieve detection limits of 0.12 and 0.03 μg L^{-1} for bromoform and chloroform, respectively.[11] Unfortunately, such analytical procedures are generally not suitable for rapid, on-site analysis; the relatively expensive instrumentation, lack of portability, and time-consuming sample preparation or detection steps are drawbacks. Hence, the development of methodology that provides for the rapid and sensitive determination of THMs in drinking water is a desirable goal.

Electrochemical methods, which are of low cost and portable, have been reported to exhibit superior performance for the determination of a wide range of pollutants in water supplies.[12,13] For these reasons, there has been considerable interest in the use of electrochemical sensors for the determination of THMs in drinking water. Electrochemical detection (and in some cases, the measurement) of organohalides, mainly THMs and other low-molecular-weight, short-carbon-chain halogenated hydrocarbons, has been performed with electrodes whose surfaces are modified with salens, porphyrins, and macrocyclic compounds,[14−17] as well as Zn metal−polytetrafluoroethylene particle (PTFE) composite-plated electrodes.[18,19]

Recently, elemental silver has been utilized as a cathode material for the reductive cleavage of carbon−halogen bonds.[20−31] Among other metals, silver has a high hydrogen overvoltage and an affinity for halide ions that result in its behaving as an electrocatalyst for the reduction of halogenated organic compounds. Silver has been employed in aqueous and nonaqueous solvents and applied to many fields, including synthetic and environmental applications. Isse and co-workers[21] have reported that the potential for reduction of chloroform shifts to a more positive value by approximately 600 mV when silver instead of glassy carbon is used as a cathode.

In this investigation, a three-step stripping analysis has been evaluated for the determination of a THM in water containing 0.010 M tetraethylammonium benzoate (TEAB) as the

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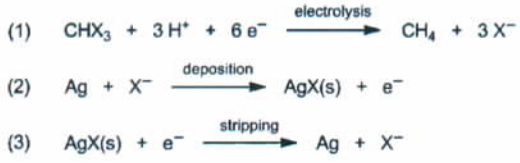
supporting electrolyte. Stripping voltammetry has been utilized for the determination of many environmental hazards such as lead and cadmium[32,33] and of pesticides at nanomolar levels.[34,35] For the first (or electrolysis) step of our procedure, a silver working cathode is used to electrolyze essentially quantitatively a THM-containing sample to release the halide ions. In the second (or deposition) step, the previously freed halide ions are collected by anodic polarization of a silver electrode to form a silver halide film that adheres to the electrode surface; the purpose of this step is to extend the detection limits to the nanomolar concentration level. Finally, the third (or stripping) step involves reduction of the silver halide film by means of differential pulse voltammetry (DPV). Then, the second and third steps are repeated—*but upon addition of a known volume of a standard bromide or chloride solution*—and the difference in the DPV signals is used to determine the original concentration of THM in the sample. This three-step protocol is depicted in Scheme 1. Because real

Scheme 1. Three-Step Stripping-Analysis Procedure to Determine THMs in Water



water samples inevitably contain free bromide and chloride (in addition to THMs and other halogenated pollutants), a preliminary step must be added to the three-step procedure. This preliminary step entails the use of a sacrificial silver anode that is employed to capture both bromide and chloride present in the original sample prior to electrolytic reduction of trihalomethanes that is represented by step 1 in Scheme 1. In fact, as indicated later in this paper, we employed this strategy for the analysis of an authentic sample of drinking water from Bloomington, Indiana.

EXPERIMENTAL SECTION

Reagents and Instrumentation. Bromoform, bromodichloromethane, dibromochloromethane, dibromomethane, bromomethane, chloromethane, tetraethylammonium benzoate (TEAB), sodium chloride, and platinum wire (1 mm diameter) were all purchased from Aldrich. Other compounds and electrode materials (with sources in parentheses) are as follows: sodium bromide (J. T. Baker); alumina (EM Science); chloroform, dichloromethane, and sodium bicarbonate (Mallinckrodt); silver slugs (6.35 mm diameter, Permion); and silver gauze (0.356 mm diameter, Alfa Aesar).

An EG&G PAR 2273 multipurpose electrochemical instrument was utilized with PowerSuite software. A stir plate was employed during the electrolysis and deposition steps. All water was obtained from a Millipore model Super Q Plus nanopure water system (>18 MΩ cm).

Electrodes and Cells. Two different electrode configurations were employed. First, to record linear-sweep voltammograms for THMs, we employed a circular silver slug (calculated geometric area = 0.317 cm^2) that was press-fitted into the bottom of a Teflon rod. Electrical contact to this electrode was achieved via a stainless steel pin that contacted the silver and extended upward through the axis of the rod. A circular groove, machined at a distance of 2 mm around the silver slug, accommodated a thin platinum wire which served as the auxiliary electrode. Second, to determine the concentrations of THMs, a silver gauze (calculated geometric area = 98 cm^2), pressed into a circle, was utilized as the working electrode, and the auxiliary electrode was a platinum wire. A homemade saturated calomel reference electrode (SCE) was used with both of the above working electrodes. Silver-slug electrodes were cleaned with sandpaper and alumina and then rinsed with distilled water in an ultrasonic bath; silver gauze electrodes were cleaned ultrasonically in a sodium bicarbonate paste, then washed ultrasonically in water, dried in an oven, and stored in a desiccator.

For all linear-sweep voltammetry experiments, a custom-made glass cell was utilized.[36] Because this study centers on the determination of halide ions at submicromolar levels, and the concentration of dilute solutions (10^{-8} M) can be lowered as a consequence of the adsorption of ionic species onto glass surfaces,[37] the cell employed for stripping analysis was made entirely of Teflon and was designed to contain a 10.0 mL sample of water.

Electrochemical Procedures. Linear-sweep voltammetry was employed to determine the reduction potentials for THMs and the potential at which a silver halide film would be deposited. In each study the scan rate was 100 mV s^{-1}, and a platinum wire and a saturated calomel electrode were employed as the auxiliary and reference electrodes, respectively. To determine the potentials for the electrolytic reduction of THMs, a silver cathode was used; the concentration of trihalomethanes as well as other less-halogenated species (dihalo- and monohalomethanes) was 5.0 mM in nanopure water containing 0.010 M TEAB as supporting electrolyte. To determine the potential needed for the anodic deposition of a silver halide film, the potential of a silver anode was varied, along with the deposition time, until a stripping peak was seen for each halide ion (Br^- or Cl^-). Three solutions were tested: (a) aqueous 0.010 M TEAB, (b) 5.0 mM sodium bromide in aqueous 0.010 M TEAB, and (c) 5.0 mM sodium chloride in aqueous 0.010 M TEAB.

As stated earlier, the stripping-analysis procedure consisted of three steps, all of which were carried out in the same electrochemical cell and with the same working (silver gauze), auxiliary (platinum), and reference (SCE) electrodes. For the electrolysis step, free halide ions were released as a well-stirred solution of a THM in nanopure water containing 0.010 M TEAB was subjected to a controlled-potential reduction for an optimized potential and time.

Differential pulse voltammetry (DPV) was utilized for both the deposition and stripping steps. Parameters for these measurements were as follows: the pulse width was 50 ms; pulse height was 25 mV; step time was 100 ms; and step height was 5 mV. To obtain the best DPV signal, the anodic preconcentration time and effective scan rate were optimized. For the anodic deposition of a silver halide film, the solution was stirred to increase the mass transport of free halide ions to the silver gauze anode. For the stripping step, the step height was changed to vary the effective scan rate from 10 to 100 mV s^{-1}. Afterward, a rest time of 5 s was observed, and then the change in current was recorded as the potential was swept to a more negative value to strip (reduce) the silver halide film.

To determine the concentration of THM in a water sample, the technique of standard addition was utilized. A single addition of a standard solution of sodium bromide or sodium

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chloride was introduced into the sample after the stripping analysis was complete to allow the original concentration of THM to be calculated. To prove the applicability of the method of standard addition, this protocol was tested with an electrolyte–nanopure water blank and with THM standards (in electrolyte–nanopure water).

RESULTS AND DISCUSSION

Electrolysis Step. To optimize the electrolysis step so that quantitative dehalogenation of a THM occurs, it was necessary to establish both the *electrolysis potential* and *electrolysis time* required for complete six-electron reduction of THMs to methane, as indicated in step 1 of Scheme 1.

Electrolysis Potential. To ensure the determination of the total trihalomethane content of a water sample, the reduction potentials for bromoform, chloroform, bromodichloromethane, and dibromochloromethane, as well as for their less-halogenated products had to be ascertained. Accordingly, cathodic peak potentials for all of these compounds are compiled in Table 1, whereas linear-sweep voltammograms for reduction of just the four trihalomethanes are depicted in Figure 1. Among the reduction products, only bromochloromethane has not been investigated by means of voltammetry; however, we would expect this compound to undergo reduction to chloromethane, which is included among the species listed in Table 1. Data presented in Table 1 reveal that, if the potential of a silver cathode is −1.40 V vs SCE, any or all of the trihalomethanes and their reduction products will undergo complete dehalogenation.

Table 1. Peak Potentials for Trihalomethanes and Their Reduction Products Obtained by Means of Linear-Sweep Voltammetry[a]

compound	peak potentials (V vs SCE)
bromoform	−0.80 and −1.15
dibromomethane	−1.06
bromomethane	−1.30
chloroform	−1.05
dichloromethane	−0.88
chloromethane	−0.80
dibromochloromethane	−0.71 and −0.98
bromodichloromethane	−0.62 and −0.98

[a]Voltammograms were recorded with a silver-slug cathode (area = 0.317 cm^2) at a scan rate of 100 mV s^{-1} in water containing 0.010 M TEAB and 5.0 mM of each compound.

Increasingly more negative potentials have to be applied to release bromide ions when there are fewer bromines on carbon; thus, reduction of bromomethane requires the most negative potential. Bromoform and dibromomethane exhibit one less peak than the number of carbon–bromine bonds. Isse and coworkers[21] found that, after the addition of one equivalent of acid to a chloroform solution, the three reduction peaks for chloroform coalesced into two cathodic peaks. For the present work, water is a viable proton donor, so the appearance of two cathodic peaks for the reduction of bromoform is not unexpected. As the number of carbon–chlorine bonds decreases, the peak potential shifts to a more positive value, which is in contradistinction to the behavior of bromoform previously described. Furthermore, chloroform has been reported[21] to show one irreversible cathodic peak at a potential more positive than that for reduction of dichloromethane. It

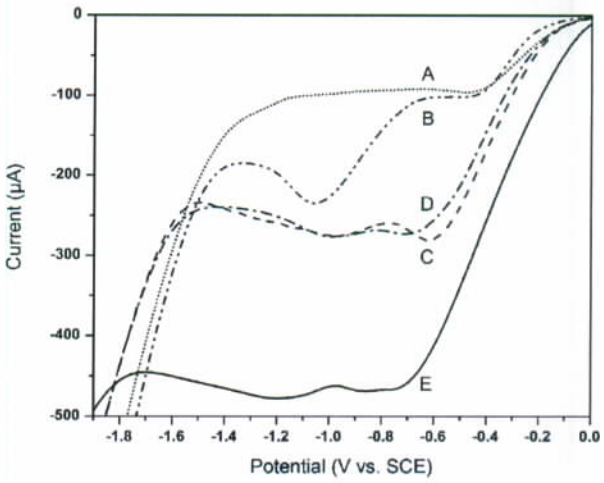

Figure 1. Linear-sweep voltammograms for reduction of trihalomethanes recorded with a silver-slug cathode (area = 0.317 cm^2) at a scan rate of 100 mV s^{-1} in water containing 0.010 M TEAB: (A) background, (B) 5.0 mM chloroform, (C) 5.0 mM bromodichloromethane, (D) 5.0 mM dibromochloromethane, and (E) 5.0 mM bromoform. All potential scans go from 0 to −1.90 V vs SCE.

should be emphasized that the purpose of Figure 1 is only to provide information about the potentials required to reduce the various THMs. If one were interested in studying the detailed electrochemical behavior of the THMs (as well as their reduction products), a more elaborate investigation of each THM in an oxygen-free medium would be necessary; such a study will be the object of future work.

Electrolysis Time. To establish that all three carbon–halogen bonds of a trihalomethane are cleaved during a controlled-potential electrolysis, three 5.00 mM solutions of bromoform were electrolyzed, and an n value of 6.34 ± 0.16 was obtained for an electrolysis time of 1000 s. Thus, this time interval was chosen for the remainder of this research. Presumably, the slightly elevated n value reflects the fact that there is some reduction of extraneous components (such as oxygen) in the system; however, deoxygenation of the solution was avoided to prevent the loss of volatile THMs. In addition, we stress here that the use of an electrolysis time of 1000 s clearly depends on parameters such as the volume of solution in the electrochemical cell and area of the working electrode (silver gauze); if the area of the electrode is increased relative to the sample volume in the cell, it is reasonable to expect that the electrolysis time can be shortened.

Deposition and Stripping Step. PowerSuite software allows the deposition and stripping steps to be combined into a single differential pulse voltammetry (DPV) experiment. Optimization of the deposition and stripping step required that three parameters—(a) *deposition potential* for the silver halide film, (b) *deposition time* for the silver halide film, and (c) *effective scan rate* for quantitative reduction of the silver halide film—be established and controlled.

Deposition Potential. To determine the potential at which silver should be oxidized to form a silver halide film, linear-sweep voltammetry was utilized. Unfortunately, there was a danger that formation of silver oxide can compete with the production of a silver halide film, leading to an erroneously high DPV signal for the subsequent measurement of the silver halide film. Accordingly, a potential had to be found at which silver

bromide or silver chloride, *but not silver oxide*, could be formed anodically.

A silver gauze anode was held at a chosen potential for 15 s before the start of each negative-going potential sweep in the water–electrolyte medium. No cathodic peak attributable to reduction of anodically formed silver oxide was detected until a threshold potential of +0.35 V vs SCE was reached. However, to obtain a cathodic peak for reduction of a silver bromide film (anodically produced in the presence of 5.0 mM sodium bromide), a potential of +0.20 V vs SCE was adequate, whereas reduction of a silver chloride film was seen at a potential of +0.25 V vs SCE. Obviously, if a solution arising from electrolytic reduction of a mixture of trihalomethanes contains both bromide and chloride, the oxidation of silver at +0.25 V vs SCE will result in the formation of a mixed silver bromide–silver chloride film. For the determination of bromoform a potential of +0.20 V vs SCE is sufficient, whereas a potential of +0.25 V vs SCE is appropriate for bromodichloromethane, dibromochloromethane, and chloroform, either individually or for a mixture of all four trihalomethanes.

Deposition Time. Detection limits for the method of stripping analysis rely on control of the deposition time for a silver halide film; thus, to achieve nanomolar detection limits, we had to optimize this deposition time. A solution of 0.90 μM sodium halide in water containing 0.010 M TEAB was utilized for repetitive differential pulse voltammetry experiments with at least four different deposition times, as summarized in Table 2.

Table 2. Optimization of Deposition Time and Effective Scan Rate[a]

deposition time (s)[a]	900	1050	1200	1350	1500
peak area after silver anode was held at +0.20 V vs SCE (μC)	3.9	34.6	68.6	101	124
deposition time (s)[a]	150	300	450	600	
peak area after silver anode was held at +0.25 V vs SCE (μC)	9.6	56.4	768	3532	
step height (mV)[b]	1	3	5	7	10
effective scan rate (mV s^{-1})	10	30	50	70	100
peak area (μC)	69.7	394	467	374	277

[a]Parameters for these measurements were as follows: pulse width = 50 ms; pulse height = 25 mV; step time = 100 ms; step height = 3 mV. [b]Parameters were the same as for preceding footnote, except that deposition time = 900 s and step height (and effective scan rate) were changed.

For a sodium bromide solution, a cathodic peak for reduction of silver bromide was first seen at a deposition time of 900 s; as the deposition time was increased, the peak area for reduction of silver bromide increased linearly (with a correlation coefficient of 0.996). Similarly, when silver chloride was deposited onto the silver anode, a stripping peak was first observed for a deposition time of only 150 s (because the deposition potential was 50 mV more positive than that used for the deposition of silver bromide), and the peak area increased with the deposition time. To minimize the overall time for the measurement of trihalomethanes in water, a deposition time of 900 s was chosen for the determination of bromoform alone, whereas 150 s was employed for each trihalomethane individually or for a mixture of all four trihalomethanes.

Effective Scan Rate. After the deposition potential and deposition time were both optimized, we selected the effective scan rate for the stripping step by using various step heights. Differential pulse voltammograms were recorded with effective scan rates ranging from 10 to 100 mV s^{-1} in a 0.030 μM sodium bromide solution containing 0.010 M TEAB. Table 2 presents the peak areas for each of the effective scan rates tested; a maximum peak area was obtained for an effective scan rate of 50 mV s^{-1} (corresponding to a step height of 5 mV). Therefore, on the basis of these observations, we chose an effective scan rate of 50 mV s^{-1}.

Analytical Performance. Once all of the optimizations were accomplished, we used the method of standard addition to analyze sample solutions of each THM individually by means of the stripping analysis protocol. Each analysis required no longer than 30 min, but this time could be shortened if the area of the silver electrode is larger. Figure 2 shows differential pulse voltammograms, corresponding to the third (stripping) step of the procedure, obtained by analysis of a 10.0 mL aliquot of a dibromochloromethane solution (left panel) and the same solution to which was added 5.0 μL of a standard 1.50 mM sodium chloride solution (right panel). Obviously, an increase in peak area (from A_1 to A_2) can be seen due to the addition of the standard. Using these peak areas, along with the known concentration (C_S) of the standard, the volume (V_S) of standard added, the final volume (V_F) of the solution, and the volume (V_O) of the original trihalomethane sample, one can obtain the original concentration (C_{THM}) of the trihalomethane from the equation

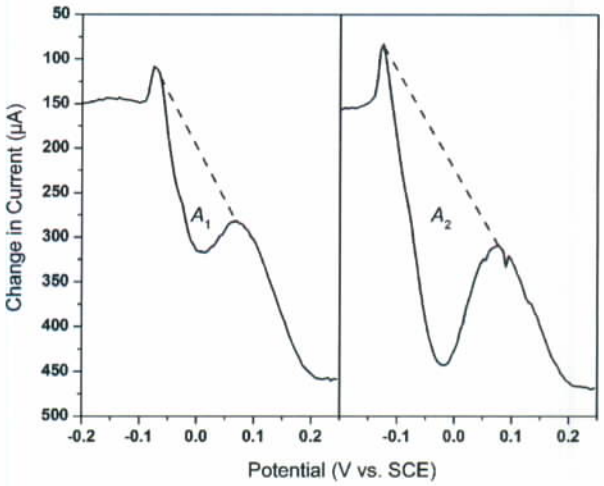

Figure 2. Differential pulse voltammograms recorded after the electrolysis step with a silver gauze electrode held at an initial potential of +0.25 V vs SCE for 150 s in 10.0 mL of an aqueous solution originally containing 34 μg L^{-1} of dibromochloromethane and 0.010 M TEAB before (left panel) and after (right panel) the addition of 5.00 μL of a 1.50 mM standard solution of sodium chloride. These curves were recorded for a pulse width of 50 ms, pulse height of 25 mV, step time of 100 ms, and step height of 5 mV. Peak areas (A_1 and A_2) are utilized for the determination of trihalomethanes in an original sample solution.

$$C_{THM} = \frac{(A_1)(C_S)(V_S)}{3[(A_2)(V_F) - (A_1)(V_O)]}$$

where the factor of 3 in the denominator reflects the fact that three halide ions are released for every molecule of trihalomethane reduced. Known and found concentrations for each of the trihalomethanes alone are displayed in Table 3. Each found

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Table 3. Comparison of Known and Found Concentrations Obtained by Means of Stripping Analysis with the Method of Standard Addition[a]

compound	known (μg L^{-1})	found (μg L^{-1})
bromoform	182	170 ± 22[b]
	113	109 ± 4[b]
	33	23 ± 7[b]
	46	51 ± 5
dibromochloromethane	103	122 ± 2
	34	31 ± 4
bromodichloromethane	147	127 ± 32
	40	39 ± 13
chloroform	125	136 ± 34
	83	90 ± 12

[a]Experimental conditions were the same as for Figure 2. [b]Parameters were the same as for preceding footnote, except that deposition potential = +0.20 V vs SCE and deposition time = 900 s.

value is the average of at least two trials with a confidence limit of 95%. At the lowest concentration tested, we acquired a signal-to-noise ratio of 95. Bromoform was determined at both deposition potentials (+0.20 and +0.25 V vs SCE) with no observable difference in accuracy. As revealed in Table 3, essentially quantitative deposition of silver bromide required 900 s when the silver anode was held at +0.20 V vs SCE, but the deposition time was only 150 s when the potential of the silver anode was +0.25 V vs SCE. Thus, in the interest of speed of analysis, it is possible to hold the potential of the silver anode at +0.25 V vs SCE for all THMs. As the chlorine content of a trihalomethane increases, its volatility also increases, and so the reproducibility of analyses suffers, which is evident for the entries in Table 3 corresponding to the measurement of bromodichloromethane and chloroform. We established the detection limits for bromoform and chloroform by applying our protocol to an electrolyte–nanopure water blank; the detection limit for bromoform was 12 nM or 3.0 μg L^{-1} at +0.20 V vs SCE, whereas the detection limit for chloroform was 50 nM or 6.0 μg L^{-1} at +0.25 V vs SCE. These detection limits are inferior to those attainable by the EPA method: 0.12 and 0.03 μg L^{-1} for bromoform and chloroform, respectively.[11] To lower these detection limits, the time for deposition of the silver halide could be lengthened, while a short total analysis time is maintained. However, in its present form, the protocol described in this report affords satisfactory results for THM levels that are commensurate with EPA requirements.

To prove the validity of our method, a mixture of all four trihalomethanes was tested by means of the stripping analysis procedure as well as by EPA method 524.2. As we are not equipped with the instrumentation needed to carry out the EPA protocol, Underwriters Laboratories, Inc. in South Bend, Indiana was contacted and agreed to determine the total trihalomethane (TTHM) content in our mixture. For our stripping analysis procedure, an identical mixture of all four trihalomethanes was added to each of three glass vials containing a known volume of nanopure water to provide a TTHM content of 52 μg L^{-1} (actually, 33 μg L^{-1} of $CHCl_3$, 10 μg L^{-1} of $CHBrCl_2$, 2 μg L^{-1} of $CHBr_2Cl$, and 7 μg L^{-1} of $CHBr_3$). Supporting electrolyte (TEAB) was dissolved in each vial. The resulting solutions were immediately analyzed according to our protocol, with all solutions being kept at ambient temperature, and we obtained an average TTHM content of 59 ± 15 μg L^{-1}. From the Underwriters Laboratories, we obtained a drinking-water-analysis kit that consisted of three glass vials containing solid ascorbic acid (used in practice to remove any residual chlorine from drinking water) and three glass vials containing hydrochloric acid (used in practice to adjust the pH of drinking water to <2). To the vials containing ascorbic acid, we added an identical volume of nanopure water along with identical mixtures of the four trihalomethanes, after which hydrochloric acid from the other vials was introduced. Immediately after being capped, the three vials containing the resulting samples were continually maintained at 4 °C while they were packaged and shipped overnight in a Styrofoam container provided with an ice pack to the Underwriters Laboratories. After being stored for three days at 4 °C, the samples were analyzed according to the EPA method, and an average TTHM content of 37 ± 10 μg L^{-1} (actually, 16 ± 2.5 μg L^{-1} of $CHCl_3$, 15 ± 8.8 μg L^{-1} of $CHBrCl_2$, 1 ± 0.3 μg L^{-1} of $CHBr_2Cl$, and 5 ± 2.2 μg L^{-1} of $CHBr_3$) was reported. Results obtained by means of the EPA method might be lower than our findings partly due to the time that elapsed between preparation of samples and their analysis by Underwriters Laboratories.

An authentic sample of drinking water from Bloomington, Indiana was analyzed in triplicate by means of our stripping analysis protocol, with provision being made to remove any free bromide and chloride originally present by means of a preliminary step that involved the use of a sacrificial silver anode held at +0.25 V vs SCE for 600 s. Using this approach, we found that a sample of drinking water obtained in 2012 had a "TTHM" content of 209 ± 23 μg L^{-1}, which can be compared with a TTHM range of 28.5–137.6 μg L^{-1} (and an annual average of 64.2 μg L^{-1}) for the year 2010 that was tabulated in the official water quality report[38] for Bloomington. However, we would like to stress the fact that our result is likely to include not only the four trihalomethanes but all halogenated species in drinking water that undergo reduction at silver at a potential of −1.40 V vs SCE. In early work aimed at the determination of haloacetic acids (HAAs) in water, we have discovered that the five EPA-regulated haloacetic acids (Cl_3CCO_2H, Cl_2HCCO_2H, ClH_2CCO_2H, Br_2HCCO_2H, and BrH_2CCO_2H) are all reducible at potentials comparable to those for the reduction of THMs, which supports the above finding that our "TTHM" content of an actual sample of drinking water was unexpectedly high. Ghernaout and Ghernaout[39] state that more than 700 disinfection byproducts arising from the chlorination of water have been reported, and that this total might account for only one-half of all halogenated organic compounds produced via chlorination. A recent review chapter by Richardson and Postigo[40] summarizes up-to-date information about regulated disinfection byproducts (trihalomethanes, haloacetic acids, bromate, and chlorite) as well as numerous families of emerging (nonregulated) disinfection byproducts. In summary, our stripping analysis protocol is not selective for trihalomethanes alone but must really be a measure of all halogen-containing species that are reducible at a silver cathode under the conditions of our procedure. Indeed, from an environmental and health perspective, knowledge of the total of reducible halogenated compounds may be valuable information to acquire.

■ CONCLUSIONS

In reality, our proposed method for the determination of trihalomethanes in drinking water more likely provides a measure of the total concentration of halide ions arising from

all halogenated compounds (trihalomethanes, other disinfection byproducts, and even pesticides, herbicides, and insecticides) that are reducible at a silver cathode under our experimental conditions. Perhaps this protocol could be used as an onsite, rapid, and simple screening method to identify samples with high concentrations of halogenated pollutants. In future work, studies of the electrochemical reduction of haloacetic acids and other disinfection byproducts identified by Richardson and Postigo[40] will be undertaken to compare their behavior with that of trihalomethanes to establish analytical methods for their determination in water samples and to explore the relevance of knowing the total concentration of these species as a measure of the true level of pollutants in drinking water.

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Notes

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REFERENCES

(1) Ivahnenko, T.; Zogorski, J. S. *Sources and Occurrence of Chloroform and other Trihalomethanes in Drinking-water Supply Wells in the United States, 1986–2001*; U.S. Geological Survey Scientific Investigations Report 2006-5015; U.S. Department of the Interior, U.S. Geological Survey: Reston, VA, 2006.

(2) Basic Information about Disinfection By-products in Drinking Water: Total Trihalomethanes, Haloacetic Acids, Bromate, and Chlorite. U.S. E.P.A.. http://water.epa.gov/drink/contaminants/basicinformation/disinfectionbyproducts.cfm#content(accessed 07/12/2010).

(3) Wright, J. M.; Schwartz, J.; Dockery, D. W. *Environ. Health Perspect.* **2004**, *112*, 920–925.

(4) Pourmoghaddas, H.; Stevens, A. A. *Wat. Res.* **1995**, *29*, 2059–2062.

(5) Horth, H. *Aqua* **1989**, *38*, 80–100.

(6) Richardson, S. D. *Anal. Chem.* **2007**, *79*, 4295–4324.

(7) Richardson, S. D. *Anal. Chem.* **2009**, *81*, 4645–4677.

(8) Richardson, S. D.; Ternes, T. A. *Anal. Chem.* **2011**, *83*, 4614–4648.

(9) Hosoya, K.; Sawada, E.; Kimata, K.; Araki, T.; Tanaka, N. *J. Chromatogr., A* **1994**, *662*, 37–47.

(10) Di Gioia, M. L.; Leggio, A.; Le Pera, A.; Liguori, A.; Napoli, A.; Siciliano, C. *Chromatographia* **2004**, *60*, 319–322.

(11) Munch, J. W., Ed.; *Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*, Revision 4.1; U.S. E.P.A.: U.S. Government Printing Office: Washington, DC, 1995.

(12) Trouwborst, R. E.; Clement, B. G.; Tebo, B. M.; Glazer, B. T.; Luther, G. W. *Science* **2006**, *313*, 1955–1957.

(13) Daniele, S.; Bragato, C.; Baldo, M. A.; Wang, J.; Lu, J. *Analyst* **2000**, *125*, 731–735.

(14) Carvalho, E. R.; Filho, N. C.; Firmino, A.; Oliveira, O. N., Jr.; Mattoso, L. H. C.; Martin-Neto, L. *Sens. Lett.* **2006**, *4*, 129–134.

(15) Ordaz, A. A.; Rocha, J. M.; Aguilar, F. J. A.; Granados, S. G.; Bedioui, F. *Analusis* **2000**, *28*, 238–244.

(16) Dobson, D. J.; Saini, S. *Anal. Chem.* **1997**, *69*, 3532–3538.

(17) Wiyaratn, W.; Hrapovic, S.; Liu, Y.; Surareungchai, W.; Luong, J. H. T. *Anal. Chem.* **2005**, *77*, 5742–5749.

(18) Wiyaratn, W.; Somasundrum, M.; Surareungchai, W. *Anal. Chem.* **2004**, *76*, 859–862.

(19) Wiyaratn, W.; Somasundrum, M.; Surareungchai, W. *Electroanalysis* **2003**, *15*, 1719–1722.

(20) Falciola, L.; Gennaro, A.; Isse, A. A.; Mussini, P. R.; Rossi, M. *J. Electroanal. Chem.* **2006**, *593*, 47–56.

(21) Isse, A. A.; Sandonà, G.; Durante, C.; Gennaro, A. *Electrochim. Acta* **2009**, *54*, 3235–3243.

(22) Rondinini, S.; Mussini, P. R.; Crippa, F.; Sello, G. *Electrochem. Commun.* **2000**, *2*, 491–496.

(23) Rondinini, S.; Mussini, P. R.; Muttini, P.; Sello, G. *Electrochim. Acta* **2001**, *46*, 3245–3258.

(24) Rondinini, S.; Vertova, A. *Electrochim. Acta* **2004**, *49*, 4035–4046.

(25) Isse, A. A.; Berzi, G.; Falciola, L.; Rossi, M.; Mussini, P. R.; Gennaro, A. *J. Appl. Electrochem.* **2009**, *39*, 2217–2225.

(26) Hori, Y.; Murata, K.; Oku, T. *Chem. Lett.* **2003**, *32*, 230–231.

(27) Ardizzone, S.; Cappelletti, G.; Mussini, P. R.; Rondinini, S.; Doubova, L. M. *J. Electroanal. Chem.* **2002**, *532*, 285–293.

(28) Durante, C.; Isse, A. A.; Sandonà, G.; Gennaro, A. *Appl. Catal., B* **2009**, *88*, 479–489.

(29) Rondinini, S.; Mussini, P. R.; Specchia, M.; Vertova, A. *J. Electrochem. Soc.* **2001**, *148*, D102–D107.

(30) Scialdone, O.; Guarisco, C.; Galia, A.; Herbois, R. *J. Electroanal. Chem.* **2010**, *641*, 14–22.

(31) Sonoyama, N.; Hara, K.; Sakata, T. *Chem. Lett.* **1997**, *26*, 131–132.

(32) Bonfil, Y.; Kirowa-Eisner, E. *Anal. Chim. Acta* **2002**, *457*, 285–296.

(33) Zhang, W.; Liu, Z.; Zhu, S.; Chen, J.; Xu, G. *Electrochem. Commun.* **2010**, *12*, 1291–1293.

(34) Liu, G.; Lin, Y. *Electrochem. Commun.* **2005**, *7*, 339–343.

(35) Li, H.; Li, J.; Yang, Z.; Xu, Q.; Hu, X. *Anal. Chem.* **2011**, *83*, 5290–5295.

(36) Vieira, K. L; Peters, D. G. *J. Electroanal. Chem.* **1985**, *196*, 93–104.

(37) Shain, I. Stripping Analysis. In *Treatise on Analytical Chemistry*; Kolthoff, I. M., Elving, P. J., Eds.; Interscience Publishers: New York, 1963; Vol. 4, Chapter 50.

(38) City of Bloomington Utilities. *Water Quality Report 2011*; Water Quality Office: Bloomington, IN, 2011.

(39) Ghernaout, D.; Ghernaout, B. *Desalin. Water Treat.* **2010**, *16*, 156–175.

(40) Richardson, S. D.; Postigo, C. Drinking Water Disinfection Byproducts. *The Handbook of Environmental Chemistry*. [online early access]. DOI:10.1007/698_2001-12_125. http://www.springerlink.com/content/a5p46k251m66176n/ (accessed 04/04/2012).