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“Development of an Automated On-line Electrochemical Chlorite Ion Sensor”

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Abstract

A sensor system for the automatic, in-line, determination of chlorite ion is reported. Electroanalytical measurements were performed in electrolyte-free liquids by using an electrochemical probe (EC), which enables in-line detection in high-resistance media such as disinfected water. Cyclic voltammetry scan rate studies suggest that the current arising from the oxidation of chlorite ion at an EC probe is mass-transfer limited. By coupling FIA with an EC probe amperometric cell, automated analysis was achieved.

This sensor is intended to fulfill the daily monitoring requirements of the EPA DBP regulations for chlorite ion. Detection limits of 0.02–0.13 mg/L were attained, which is about one order of magnitude below the MRDL. The sensor showed no faradaic signal for perchlorate, chlorate, or nitrate. The lifetime and stability of the sensor were investigated by measuring calibration curves over time under constant-flow conditions. Detection limits of <0.1 mg/L were repeatedly achieved over a period of three weeks.

Introduction

The main purpose of water disinfection is to limit waterborne disease and inactive pathogenic organisms. Disinfectants tend to be strong oxidants or species that generate oxidants as byproducts (1). Chlorine is the most widely used disinfection agent in United States public drinking water treatment because it is a very effective biocide; however, the process results in chlorinated organic disinfection by-products (DBP) such as trihalomethanes (THM) and haloacetic acids (HAA) (1). The DBPs produced through water chlorination and the ensuing EPA regulations have led to an increased interest in disinfectants other than chlorine. The most popular alternatives are listed in the Alternative Disinfectants and Oxidants Guidance Manual (1); they are ozone, chlorine dioxide, potassium permanganate, chloramine, ozone/hydrogen peroxide combinations, and ultraviolet radiation.

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Chlorine dioxide (ClO_2) is a popular alternative to chlorine for water treatment because it disinfects over a wide pH range without chlorinating organic molecules (2). One of the pressing concerns about chlorine dioxide is the formation of chlorite ion because it can potentially cause hemolytic anemia and adverse nervous system effects (3). The United States EPA has regulated a 1 mg/L maximum contaminant level (MCL) for ClO_2^- ion in drinking water. Consistent with this restriction, EPA regulations state that facilities that use chlorine dioxide for water disinfection must monitor daily chlorite ion and chlorine dioxide concentrations in the water. The EPA 40 CFR §141.131(b) states that chlorite ion must be monitored with Amperometric Titration Standard Method 4500- ClO_2^- E or Ion Chromatography EPA Method 300.11; the EPA 40 CFR §141.131(c) states that ClO_2 must be monitored using DPD Standard Method 4500- ClO_2 D or Amperometric Method II Standard Method 4500- ClO_2 E.

The EPA standard methods for monitoring chlorite ion have characteristics that are not compatible with incorporation into automated, in-line monitoring systems. These problems make compliance with EPA chlorite ion regulations burdensome. A possible solution is to develop an automated, in-line chlorite ion sensor. Automated analysis would simplify the monitoring process by obviating manual sample collection, sample preparation, and batch analysis (4).

The concerns about existing standard methods focused this research on the development of a new method that meets the in-line requirements and exhibits equivalence in analytical figures-of-merit to the standard methods. However, before any analytical method can be developed, it is imperative that we understand the chemistry of the chemical species. In this case the method must differentiate among numerous oxy-chlorine species.

ClO_2 is an energetic oxidizing agent that has a high solubility in dilute aqueous solutions where it exists as a free radical (5) and a volatile dissolved gas. Oxidation primarily occurs through a selective one-electron transfer mechanism where ClO_2 is reduced to chlorite ion (ClO_2^-). When ClO_2 is used under typical conditions for water disinfection, approximately 50-70% gets converted to chlorite ion and 30% to chlorate ion (1). Organic DBPs are produced when ClO_2 reacts with biological material. Chlorite ion is stable in the presence of the organic DBPs (1) but can be oxidized to chlorate ion under basic conditions in the presence of free chlorine, which is used as a secondary disinfectant. Richardson et al. (6) found that although there are more than 40 different semi-volatile, organic DBPs produced from ClO_2 disinfection, their concentrations were negligible in practical applications (approximately 1-10 ng/L).

The reduction potential of the $\text{ClO}_2^-/\text{ClO}_2$ couple is the lowest in the oxy-chlorine species redox series (Table 1).

Based on these redox potentials electrochemical sensors are promising candidates for monitoring chlorite ion given their low cost, fast response times, ease of miniaturization, and stability (7). In addition, electrochemical detection is relatively easy to automate due to advances in flowthrough electrochemical detectors for FIA and capillary electrophoresis (8). The in-line electrolytic measurement of oxy-chlorine species in drinking water, however, is difficult due to low electrolyte concentrations in disinfected water. Even the approved amperometric method has some difficulties with the measurement of chlorite ion pure drinking water. Therefore, one goal of this study is to address the challenge of making direct amperometric measurements on samples that do not contain sufficient electrolyte to suppress migration of the analyte.

Prior electrochemical studies of the oxidation of ClO_2^- have suggested that it undergoes a diffusion-limited, one-electron oxidation. In 1967, Schwarzer and Landsberg reported that

the oxidation of chlorite ion on graphite rotating disk electrode in the pH range 5-9 produced a current that was proportional to concentration (9). Raspi and Pergola later investigated the reversibility of the redox couple using a platinum microelectrode (10). They reported a $\log[i/(i_d - i)]$ vs. E plot showing a straight line with a slope of about 60 mV, which is consistent with a reversible, one-electron transfer reaction. The most thorough investigation of the electrochemistry of chlorite ion was performed by Sinkaset and Trogler using rotating disc and ac voltammetry to measure the heterogeneous rate constant (k_{el}) (11). The reported cyclic voltammogram of chlorite ion had a ΔE_p of ~ 70 mV and an anodic-to-cathodic peak current ratio of ca. 1.0. The k_{el} of the reaction was 0.014 ± 0.003 cm/s on a platinum electrode. The heterogeneous rate constant was not appreciably affected by proton concentration when the pH was above 5. The kinetic experiments suggested that the heterogeneous electron transfer of chlorite ion oxidation is electrochemically reversible.

Casella recently reported the use of silver nano-islands grown on a glassy carbon electrode to electrochemically reduce chlorite (12). The surface showed resistance to surface poisoning, but no detection limits were given and the response times were high (6-8 s) (12). In previous work, a tungsten oxide electrode was used as an amperometric sensor for ClO_2^- with a detection limit of 0.027 mg/L (13). Ohura and Yamasaki developed a potentiometric FIA technique that was able to simultaneously determine ClO_2^- ion and ClO_3^- (14). A potential change was observed at a redox electrode based on reaction of the oxy-chlorine species with a Fe(III)-Fe(II) buffer; however, ClO_2^- ion interfered with the measurement if its concentration was higher than that of ClO_3^- . Pezzatini and Innocenti used pulse voltammetry with a carbon electrode to investigate the oxidation of ClO_2^- to ClO_2 (15). Although the detection limit, 0.07 mg/L, was comparable to that of ion chromatography with a conductivity detector, the electrode required extensive polishing and electrochemical pretreatment prior to measurements, a factor that precludes this approach from consideration as an in-line sensor.

In order to address the low electrolyte problem, housing the electrodes in a sol-gel based matrix was identified as potential sensor design. The sol-gel process is a wet chemical technique used to make three-dimensional inorganic macromolecular networks (16). The versatility of the process enables precise control of microstructure and bulk shape, resulting in solid materials with welldefined composition, morphology, and porosity. In addition, organic components can be incorporated into the network to create organic-inorganic hybrids that combine the rigid threedimensional inorganic architecture with easily accessible active sites in the pores of the material (17). Tailoring the chemical, mechanical, optical, and electrical properties of these materials has found numerous applications in analytical chemistry, such as chemical and biological sensors, stationary phases for chromatography, anti-reflective coatings, and electrode modifiers (16).

Interest in sol-gel processing of supported thin films has grown considerably in recent years due to numerous applications of patterned, nanostructured materials in optical, electronic, electrochemical and sensing devices (17). One of the key developments that allowed electrochemical measurements in matrices comprised of sol-gels was processing in the presence of surfactants at levels well above their critical micelle concentrations (18). The resulting mesoporous solid allows facile diffusion of electroactive species therein. For example, the effective diffusion coefficient of iron hexacyanoferrate in a mesoporous silica sol-gel derived from tetramethyl orthosilicate in the presence of Triton-X 114 was $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ which is near the value of diffusion coefficients of typical electroactive species in aqueous electrolytes (19).

Widera and Cox (20) reported a method for voltammetric measurements in electrolyte-free liquids that was based on facile charge transport in mesoporous sol-gels. A silica sol-gel thin

film with templated mesopores that were doped with electrolyte served as charge-transport bridge among three electrodes that were imbedded therein. The need for a conducting path in the contacting liquid sample was thereby obviated. The working electrode contacted the liquid sample, and the electrochemical reaction occurred at the three-phase boundary (3PB) comprising the junction of the working electrode, sol-gel electrolyte and the sample-containing liquid phase. It was hypothesized that the negative silanyl groups on the silica backbone minimized leaching of the electrolyte from the pores of the sol-gel into contacting liquid phases by binding the cation by ion exchange.

The primary goal of the present study is to develop an alternative method to the EPA standard methods for chlorite ion monitoring by incorporating the sensor into an in-line, continuous monitoring system. To reach this goal, an electrochemical ClO_2^- sensor that couples flow injection analysis (FIA) automation with in-line electrochemical detection was designed and tested. The electrochemical flow cell integrates a 3PB electrode into a FIA flow system for inline, amperometric detection in drinking water without added electrolyte. The main hypothesis is that the ClO_2^- concentration in drinking water can be amperometrically measured with the sol-gel based electrochemical probe, and a degree of selectivity can be attained via potential control. Because of its standard reduction potential, ClO_2^- is expected to oxidize at the lowest potential of all the oxy-chlorine species present in a ClO_2^- disinfected drinking water sample.

Experimental

Reagents

The precursor to the silica sol-gel was tetraethyl orthosilicate (TEOS), 99.999% purity, obtained from Sigma Aldrich Chemical Company (Milwaukee, WI). House-distilled water, which was deionized with a Millipore Milli-Q Advantage A10 system, and Spectrophotometric Grade ethanol (Aldrich) were used as co-solvents in the preparation of the silica. The surfactant template used in the preparation of the silica was Triton X-114 (Sigma Chemical Co., St Louis, MO). Ammonium hexafluorophosphate, >95% purity (Aldrich), was doped as an electrolyte into the silica during gelation. The analyte was sodium chlorite that was purified as reported by Gordon and coworkers (21). The platinum wire for the electrodes was 0.2 mm (diameter) from Sigma. All glassware was chemically pretreated prior to use to remove chlorine demand. All glassware was washed with soap and water followed by a 24 hour soak in ~1 v/v % HNO_3 . Subsequently, the glassware was soaked in dilute Clorox bleach for at least 24 h and rinsed with water just prior to use.

Probe Fabrication

Figure 1 shows the cell design of the EC probe. Platinum wires (0.2 mm dia.) composed the working (WE), counter (CE), and quasi-reference electrodes (QRE). The electrodes were supported in a 0.6-cm outer diameter (OD), 0.4-cm inner diameter (ID) plastic tube filled with an epoxy resin made by mixing EPO-TEK 353ND Part A and Part B (Epoxy Technology, Inc) in a 10:1 ratio by weight. The epoxy was cured for 30 minutes at 80°C, after which the surface was smoothed with 400-grit sandpaper. The counter and reference electrodes were coplanar with the surface of the epoxy, whereas the working electrode protruded above this plane. The three electrodes were electrochemically pretreated prior to sol-gel deposition by scanning the potential from -1.0 to 1.0 V vs. Ag/AgCl at 0.1 V/s in 0.1M H_2SO_4 . The plane was then coated with a silica sol-gel film that contained ammonium hexafluorophosphate, which was cast from 5 μL of sol. The sol consisted of 0.1 mL of TEOS, 9.0 mL of ethanol, 1.0 mL of water, 0.6 mL of water saturated with NH_4PF_6 , and 0.2 mL of Triton X-114. The sol was magnetically stirred for 2 h prior to use for film formation. The gelation time was seven days under ambient laboratory conditions. A portion of the

working electrode and all surfaces of the reference and counter electrodes were coated with silica sol-gel using this procedure. All electrochemical measurements were made with a Model 650C electrochemical workstation from CH Instruments (Austin, TX). All potentials were measured and reported vs a Pt quasi-reference electrode unless otherwise indicated.

FIA System

The flow system consisted of a syringe pump connected to a Rheodyne 7125 6-port, syringe-loading injection valve with a 250 μL external sampling loop. No additional coils are required. The detector used was an electrochemical flow cell produced by inserting the protruding portion of the EC probe's working electrode directly into the downstream flow from the injector in a wall-jet configuration. The carrier stream was deionized water. The flow rate of the carrier stream was 0.8 mL/min unless otherwise indicated. The flow system used 0.5-mm-i.d. flexible PVC tubing. Current-time curves were recorded at constant potential in the flow system. The resultant peak heights were measured using GRAMS/32AI software (version 6.0). The response time was 3 sec from injection to peak initiation. Peak width would vary depending on the volume of the sample loop used.

Results and Discussion

Cyclic voltammetry of chlorite ion was performed at a platinum electrode in a conventional three-electrode cell with a pH 10 buffer as the supporting electrolyte and with the described EC probe where the platinum electrode was embedded in a sol-gel. In the latter case, supporting electrolyte was not added to the aqueous sample. Substituting 50 mM chlorate or perchlorate ions for chlorite ion could not be distinguished from the deionized water background. In the conventional cell (Figure 2 top), the peak separation, 98 mV, and the anodic-to-cathodic peak current ratio, 1.04, agreed with a previous report of general reversibility (11), including the absence of a coupled chemical reaction on the time scale of the experiment. The Pt working electrode was treated by evolution of H_2 at -2.0 V to reduce any oxide of Pt in that the reduction of chlorite was demonstrated to be sensitive to the condition of the Pt surface (11).

At the sol-gel based EC probe in the absence of supporting electrolyte, the reduction of chlorite and the reverse of this electrochemical process are observed; however, a peak for the reduction is not developed (Figure 2 bottom). Cathodic pretreatment of the Pt electrode by H_2 evolution was not performed because of potential damage to the 3PB, so this departure from ideal reversible behavior is likely due to the presence of an oxide of Pt at the working electrode surface. Nevertheless, the reduction of chlorite at the EC probe is suited for use in an analytical method in that the current is controlled by diffusion. This point was demonstrated by investigating the current as a function of scan rate, v (Figure 3). A plot of the cathodic current at 0.2 V vs. $v^{1/2}$ is linear, which is diagnostic for linear diffusion control of the electrode process. Specifically a least squares fit of the data in Figure 3 over the v -range 20 -120 mVs^{-1} gave $R^2 = 0.99$. Of importance is that the demonstration of a linear diffusion controlled current precluded other factors that, if present, would have compromised analytical measurements at the probe, namely current limited by electron-transfer kinetics, migration, or an uncontrolled process contaminating the Pt surface.

To evaluate the EC probe for the determination of chlorite in water in the absence of supporting electrolyte, it was incorporated into the FIA system. The EC probe was tested as an FIA detector initially by five replicate 350- μL injections of 1.0 mg $\text{ClO}^- \text{L}^{-1}$ into electrolyte-free water flowed at 0.8 mL min^{-1} . The peak heights were $13.75 \pm 0.05 \text{ nA}$, and the widths were ca. 2 min. This FIA system was optimized by variation of the flow rate. When 0.2 V was the applied potential the %RSD values at 0.7, 0.8, 0.9, 1.0, and 1.1 mL

min^{-1} were 2.5, 0.75, 2.1, 4.0, and 2.8%, respectively. Hence, 0.8 mL min^{-1} was selected for subsequent measurements.

The applied potential was optimized using hydrodynamic voltammetry by measuring the current at the EC probe as a function of applied potential using FIA with a flow rate of 0.8 mL min^{-1} . The beginning of the limiting-current plateau region of the hydrodynamic voltammogram, $\sim 0.5 \text{ V}$, was used as the applied potential (Figure 4). Potentials greater than 0.51 V vs the quasi-reference electrode was not applied because of the onset of the oxidation of water, which acidified the interface. The generation of even small amounts of hydrogen ion in the diffusion layer of the electrode via the oxidation of water can have an influence on the electrochemistry of a targeted species when the contacting phases are not buffered. Therefore, an applied potential of 0.50 V was selected for further work.

The sensitivity of the optimized FIA system with an EC probe detector for the determination of chlorite in the low mg/L range was evaluated by recording calibration curves of peak height vs. concentration over the range of 0.3 to 5 mg/L (Figure 5). Linear least squares fit of the data (5 points) yielded the following: slope, $6.86 \text{ nA / mgL}^{-1}$; y-intercept, -0.55 ; and R^2 , 0.99 . The noise was quantified as the standard deviation of the intercept when all points were plotted. We hypothesize that the primary source of noise is probably the movement of the small diameter wire working electrode which is manipulated by laminar flow at the EC probe surface. Again the EC probe is placed in a wall jet configuration. The detection limit ($k = 3$ criterion) was 0.08 mg/L .

The selectivity of the detector was evaluated using three samples that contained 1.0 mg L^{-1} of one of the following anions: nitrate, chlorate, or perchlorate. The FIA measurements with 0.44 V applied showed 1-nA peaks in each case. Given that these peaks were the same for all the salts tested, the current is not related to a faradaic process. A likely cause is a change in the double layer capacitance when the plug of sample contacts the working electrode. Presuming chlorite ion will change the double layer capacitance to the same degree as these test interferences, the quantitative results will not be affected; the concomitant change in capacitive current will instead influence the intercept of the calibration curve.

The accuracy of the developed method was evaluated by measuring the concentrations of two spiked validation standards (A and B) and then comparing the results with ion chromatography (IC) (Table 2). The concentrations of the validation standards that were obtained at the probe were not significantly different at the 95% confidence level from the accepted values. Likewise, the values obtained with the EC probe and from ion chromatography were not significantly different from the validation standards at this confidence level.

The reproducibility of the sensor was evaluated by cyclic voltammetry of 44 mM chlorite ion at 100 mVs^{-1} in the absence of added electrolyte. Three probes were fabricated and tested. The anodic current at 0.40 V was $59 \pm 8 \mu\text{A}$. The limiting factors on the reproducibility of the measurement were attributed to a change in the true potential of the working electrode caused by variation of the potential of the platinum quasi-reference electrode and changes in the effective area of the working electrode. The former problem is exacerbated by the absence of a peak for the oxidation of chlorite at the probe (see Figure 4). In the latter case, the 3PB is not the true area; instead, the effective area includes that portion of the working electrode that is coated with a film of sol-gel sufficiently thinner than ca. $(Dt)^{1/2}$ where D is the effective diffusion coefficient of chlorite in the sol-gel and t is the time of contact of the plug of sample to the working electrode. In that the linear dynamic range is not altered, these factors only limit the method by requiring a sensitivity determination for each probe that is fabricated.

The day-to-day and the long-term stability of the sensor were tested by plotting calibration curves over a 19-day period. During this time the water content of the sol-gel was maintained by constant flushing with a low flow rate of deionized water. As detailed in Table 3, the slope varied between 9.6 and 13 nA·L·mg⁻¹ and the detection limit (k=3 criterion) ranged from 0.02 to 0.13 mgL⁻¹ over this period. The change in slope and the variation of detection limit fluctuated rather than vary systematically. These data suggest either employing the standard addition method for determining the sensitivity of a probe on a daily basis.

Presently we are refining the design of the EC probe. The major approaches are introducing a true reference electrode such as Ag|AgCl and controlling the wetting of the working electrode by the sol during the gelation step by chemically modifying the Pt surface.

Conclusions

A sensor system for the automatic, in-line, determination of chlorite ion is reported. Electroanalytical measurements were performed in electrolyte-free liquids by using an EC probe, which enables in-line detection in high-resistance media such as disinfected water. Cyclic voltammetry scan rate studies suggest that the current arising from the oxidation of chlorite ion at an EC probe is mass-transfer limited. By coupling FIA with an EC probe amperometric cell, automated analysis was achieved. The optimized parameters of the flow system and detector were a flow rate of 0.8 mL/min and an applied potential of 0.5 V.

This sensor is intended to fulfill the daily monitoring requirements of the EPA DBP regulations for chlorite ion. Detection limits of 0.02-0.13 mg/L were attained, which is about one order of magnitude below the MRDL. The sensor showed no faradaic signal for perchlorate, chlorate, or nitrate. Concentrations of spiked validation standards of this electrochemical method and ion chromatography were not statistically different at the 95% confidence level and accuracy was demonstrated by comparison to concentrations of standards. The lifetime and stability of the sensor were investigated by measuring calibration curves over time under constant-flow conditions. Detection limits of <0.1 mg/L were repeatedly achieved over a period of three weeks.

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Highlights

We took advantage of the order of the electrochemical potentials of the oxychlorine species to produce a sensor;

- that is selectivity for chlorite ion;
- that is not affected by electrolyte concentration in the in-line flow system;
- the electrochemical probe is based on sol-gel chemistry; and
- the sensor system compared well to the approved ion chromatography method.

Figure 1. Diagram of EC probe Design A: Sol Gel, B: Tygon tubing, WE: platinum wires (0.2 mm dia.) working electrode, CE: counter electrode, and QRE: quasi-reference electrode.

Figure 2.

Top Cyclic voltammogram of 50 mM ClO_2^- at a platinum disk electrode; Scan rate 50mV/s; pH 10.2. Bottom Cyclic voltammogram of 44.1 mg/L ClO_2^- at an EC probe; scan rate 100 mV/s pH 10.1.

Figure 3.
Scan rate studies at an EC probe; 44.1 mg/L CLO_2^- ; scan rates 20 - 120 mV/s.

Figure 4.
Hydrodynamic voltammogram data of 2.5 mg/L ClO_2 at an EC probe detector.

Figure 5. Flow Injection peaks using an EC probe ($n=5$) for 0.31, 0.63, 1.25, 2.5, and 5.0 mg/L; applied voltage 0.50 V.

Table 1

Redox reactions and standard reduction potentials of the oxy-chlorine species.

Oxy-chlorine Species	Reactions (oxidation)	Potential (V)
ClO^-_2	$\text{ClO}^-_2 \rightleftharpoons \text{ClO}_2 + \text{e}^-$	-0.954
ClO_2	$\text{ClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{ClO}^-_3 + 2\text{H}^+ + \text{e}^-$	-1.152
ClO^-_2	$\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{ClO}^-_3 + 3\text{H}^+ + 2\text{e}^-$	-1.214
ClO^-_3	$\text{ClO}^-_3 + \text{H}_2\text{O} \rightleftharpoons \text{ClO}^-_4 + 2\text{H}^+ + 2\text{e}^-$	-1.189
ClO_2	$0.5\text{Cl}_2(\text{g}) + 3\text{H}_2\text{O} \rightleftharpoons \text{ClO}^-_3 + 6\text{H}^+ + 5\text{e}^-$	-1.470
Cl_2	$0.5\text{Cl}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{H}^+ + \text{e}^-$	-1.611
ClO^-	$\text{HClO} + \text{H}_2\text{O} \rightleftharpoons \text{HClO}_2 + 2\text{H}^+ + 2\text{e}^-$	-1.645
Br^-	$\text{Br}^- + 6\text{OH}^- \rightleftharpoons \text{BrO}^-_3 + 3\text{H}_2\text{O} + 6\text{e}^-$	-0.610

Table 2

Comparison of validation standard concentrations determined with ion chromatography and the developed method. $\bar{x} \pm \sigma$ (n=3). $\bar{x}$, mean; σ , standard deviation; s_m , standard deviation of the mean.

Validation Standard	Accepted value (mg/L)	IC method	EC method
A ($\bar{x}_m \pm \sigma$)	0.250	0.253 ± 0.007	0.246 ± 0.010
B ($\bar{x}_m \pm \sigma$)	0.876	0.867 ± 0.004	0.857 ± 0.024
A($\bar{x}_m \pm t^* s_m$)	0.250	0.253 ± 0.017	0.246 ± 0.025
B($\bar{x}_m \pm t^* s_m$)	0.876	0.867 ± 0.010	0.867 ± 0.060

Table 3

Parameters for calibration curves measured on days one, two, five, nine, ten, and nineteen after EC probe fabrication.

Day	Slope (A/mgL ⁻¹)	Intercept	R ²	DL (mgL ⁻¹)
1	1.13E-08	4.55E-10	0.99	0.02
2	1.07E-08	-8.12E-11	0.99	0.04
5	9.70E-09	-6.06E-10	0.99	0.12
9	9.55E-09	1.65E-10	0.99	0.04
10	1.19E-08	-3.72E-10	0.99	0.08
19	1.29E-08	3.24E-11	0.99	0.13