

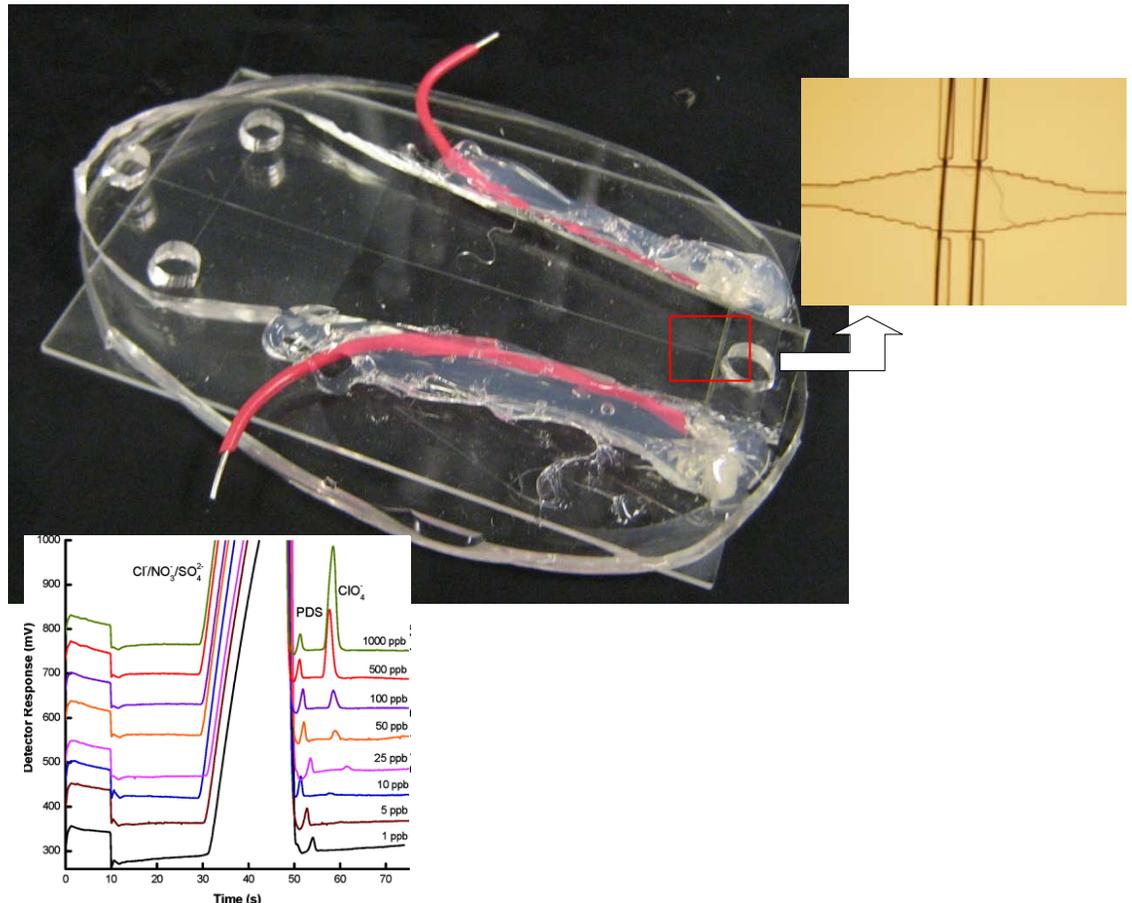


Strategic Environmental Research and Development Program ER-1706

Lab-on-a-Chip Sensor for Monitoring Perchlorate in Ground and Surface Water

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Abstract

Perchlorate is a pervasive water contaminant that has drawn national attention as a public health concern. Although perchlorate contamination has both natural and anthropogenic origins, its recurrent use in military munitions makes perchlorate the highest-priority military pollutant. Currently, perchlorate detection at the critical parts-per-billion level requires large, sophisticated instrumentation in a centralized laboratory. This report describes a fieldable, microchip capillary electrophoresis (MCE) device that is selective for perchlorate and exhibits reduced analysis times and reagent consumption. The device employs contact conductivity detection and zwitterionic surfactant chemistry to selectively resolve perchlorate from abundant environmental species such as chloride, nitrate, and sulfate. The prototype MCE system is capable of detection limits of 3.4 ± 1.8 ppb in standards and 5.6 ± 1.7 ppb in drinking water. Additional work modified the microchip geometry and separation chemistry, to account for higher ionic strength sample matrices such as surface and ground water, which cause interferences with perchlorate detection. A novel extraction method, incorporating the fundamentals of electrostatic ion chromatography (EIC), is presented as a way to overcome this challenge. Two extraction formats, employing either a packed bed or a monolith, were also investigated and presented in this work.

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Preface

This study was conducted for the Strategic Environmental Research and Development Program (SERDP) under Environmental Restoration (ER) Project ER-1706 “Lab-on-a-Chip Sensor for Monitoring Perchlorate in Ground and Surface Water.” The technical monitor was Dr. Andrea Leeson, Program Manager for Environmental Restoration at SERDP.

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), U.S. Army Engineer Research and Development Center – Construction Engineering Research Laboratory (ERDC-CERL). At the time of publication, Debbie Curtin was Chief, CEERD-CN-E; John Bandy was Chief, CEERD-CN; and Alan Anderson was the Technical Director for Environmental Quality. The Deputy Director of ERDC-CERL was Dr. Kirankumar Topudurti and the Director was Dr. Ilker Adiguzel.

COL Kevin J. Wilson was the Commander and Executive Director of ERDC, and Dr. Jeffery P. Holland was the Director.

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Unit Conversion Factors

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1 Introduction

1.1 Background

Perchlorate is a water-soluble, inorganic anion that is commonly found in food and water supplies across arid regions of the United States. Numerous sources of perchlorate have been identified, ranging from naturally occurring Chilean nitrate fertilizers to manmade sources such as military munitions. When ingested, perchlorate has known ill-health effects, specifically inhibition of normal hormonal and developmental processes by hindering the uptake of iodine in the thyroid.

Reported releases of perchlorate have occurred in at least 21 US states, and contamination is known to exist at many US Army facilities and suspected at many more. States are adding the anion to current permits, and federal and state authorities have pressured Army installations to take action through interim action levels and health advisories. Although the US Environmental Protection Agency (USEPA) has not set regulatory levels of perchlorate in drinking water, it issued an Interim Drinking Water Health Advisory in 2008 that determine a level of 15 parts per billion (ppb) is protective of all subpopulations (USEPA 2008).

Perchlorate is one of the more persistent byproducts generated in the manufacture and use of military munitions. Military munitions, along with the aerospace industry, have been linked to more than 65% of all perchlorate in ground and surface waters (Kirk 2006; US GAO 2005). Perchlorate currently is listed as the number-one emerging contaminant of Department of Defense (DoD) concern, based on a recent survey¹ sponsored by the Office of the Assistant Deputy Under Secretary of Defense for Installations and Environment (DUSD I&E) and the Range Commanders' Council (RCC).

Perchlorate is the highest-priority military contaminant due to its ubiquitous nature, persistence, and aqueous solubility. As ammonium perchlorate (AP), perchlorate is the prime oxidizer in most solid missile and rocket fuels. As potassium perchlorate (KP) and AP, perchlorate is used in

¹ Information is available on the DENIX website,
<http://www.denix.osd.mil/cmrm/ECMR/Perchlorate/TheBasics.cfm>

many pyrotechnic formulations for simulators, smokes, initiators, etc. The anion is persistent in the environment, binding weakly to soil and able to travel quickly to groundwater where it is soluble, stable, mobile, and lasting. Detection of perchlorate has occurred at Massachusetts Military Reservation (MMR); Red River Army Depot (RRAD), TX; Aberdeen Proving Ground (APG), MD; and Longhorn Army Ammunition Plant (LHAAP), TX. In addition, perchlorate has been found in ground and surface waters of attendant training ranges and open-burning/open-detonation (OB/OD) sites at APG; LHAAP; MMR; RRAD; Fort Wingate, TX; Fort Meade, MD; Picatinny Arsenal, NJ; Camp Navajo, AZ; and Lone Star Army Ammunition Plant (LSAAP), TX.

In fact, a survey initiated by SERDP² has identified perchlorate as the contaminant most likely to cause future concerns at 50% of the responding installations and is one of only five chemicals on the DoD Action List. The presence of perchlorate in drinking water has become a significant enough concern that many reports have appeared in the mainstream media. Restrictions in the use of existing bomb simulators, smokes, flares, and other perchlorate-containing pyrotechnics due to these concerns would greatly impact or potentially impede Army training.

1.1.1 Existing analysis methods

The most common methods for perchlorate detection are ion chromatography (IC) coupled to conductivity detection (CD), and IC coupled to mass spectrometry (MS) (Wagner et al. 2003). IC coupled to conductivity detection dominates environmental analytical chemistry because the limit of detection (LOD), when combined with suppressed conductivity detection, has been reported as low as 0.77 ppb using widely available instrumentation. When positive identification of perchlorate must be made, IC coupled to MS must be used where even lower limits of detection (0.02–0.005 ppb) are possible. While these two methods are capable of isolating and detecting perchlorate, the necessary instrumentation size, complexity, and cost will limit their use to laboratory-based measurements.

In the typical water-monitoring case, samples are sent to a centralized laboratory at a significant cost (up to \$200/test) with a 2–3 week turnaround time. Although the cost for a single test is not prohibitive, when

² Information is available on the Environmental Restoration portion of the SERDP website, <http://www.serdp-estcp.org/Program-Areas/Environmental-Restoration>

large numbers of samples are analyzed the total cost can become prohibitive. For these reasons, many groups have sought to develop alternative analytical methods for detecting perchlorate. Techniques explored include capillary electrophoresis (CE) with ultraviolet (UV) detection (Wang et al. 2003), infrared spectroscopy (ATR-FTIR; Hebert and Brazill 2003) and Raman spectroscopy (Agirregabirra et al. 2006). While these methods have some advantages, they generally lack the sensitivity required for routine monitoring and/or are based on large laboratory instrumentation. For these reasons, inexpensive, sensitive, portable, and compact analyzers are needed that allow continuous monitoring of perchlorate in ground water in a sentinel mode of operation.

1.1.2 Lab-on-a-chip sensors

Over the last two decades, the development and use of LOC sensors³ has become a major new thrust in the analytical field. This class of sensors offers the potential for vast improvements in analysis time and cost while also holding the promise to integrate all functions of a traditional chemical laboratory onto a single small microchip that can be installed at critical monitoring loci. Most of the effort in this area has been placed on samples of biological origin. This work has extended this field to the analysis of environmental samples.

LOC devices offer the potential to integrate all steps of a chemical analysis method into a single inexpensive package that works autonomously, but few are plausible for the analysis of low-abundance environmental contaminants. Previous efforts by the principal investigative team have established one variant of LOC technology—microchip electrophoresis—as a viable sensing option for perchlorate at the sub-parts-per-billion level when samples contain low concentrations (sub-parts per million) of interfering ions. When perchlorate water samples containing high levels of chloride and nitrate were tested, nonlinear calibration curves were required and accuracy was greatly diminished. Here, a novel extraction chemistry that uses zwitterionic surfactants was immobilized on either a conventional or membrane-based stationary phase (electrostatic ion chromatography) embedded at the injection end of a microfluidic device to extract and concentrate perchlorate from contaminated water samples prior to analysis by microchip electrophoresis/contact conductivity. Zwitterionic surfactants can selectively bind anions based on their interaction with the central cationic

³ LOC sensors are also called miniaturized total analysis systems (TAS).

onic group for betaine-type surfactant molecules. These properties were studied to identify specific surfactants' selective affinity towards perchlorate. The method reported here combines the use of contact conductivity detection, incorporating a recently reported bubble cell design (Noblitt and Henry 2008), which allows for low limits of detection and fast analysis times (approximately 1 min), with optimized separation chemistry. Two zwitterionic sulfobetaine surfactants, N-Hexadecyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (HDAPS), and N-Tetradecyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (TDAPS), were investigated for the selective retention of perchlorate. At concentrations of these surfactants above the critical micelle concentration (CMC), micellar interactions slow the migration of perchlorate, separating the analyte from common, higher mobility anions such as chloride, sulfate, and nitrate found in water. It was found that TDAPS provided more reproducible results than HDAPS. This novel separation chemistry was used to analyze for perchlorate in drinking water samples with 99% recovery and detection limits of 5 ppb.

Further, the MCE system was improved to overcome the challenges of analyzing surface and ground water in which ionic strength is substantially higher than that of drinking water. A novel extraction method incorporating the fundamentals of electrostatic ion chromatography (EIC) was proposed. Two strategies were explored for this extraction method—a reverse-phase packed bed and an in situ-generated monolith. With both strategies, a zwitterionic surfactant is physisorbed on the surface of either the packed bed or monolith. When a high ionic-strength water sample is introduced, perchlorate is retained by the surfactant while the higher concentrations of chloride, nitrate, sulfate, etc. are rinsed off the column. Perchlorate is then eluted separately and can be analyzed via MCE.

The combination of this perchlorate-affinity chemistry with LOC detection devices will have many benefits over existing approaches to create sentinel structures for real-time automated determinations of perchlorate in the environment. First, it will be faster than existing methods by giving analysis times of less than 10 min as opposed to the days currently required to collect, ship, and analyze samples in a central laboratory. Second, it will be cheaper than existing methods since labor is curtailed and inexpensive instrumentation can be used (one dollar versus hundreds of dollars per sample). Third, the designed system will have even lower limits of detection due to the concentration effect of the immobilized surfactant chemistry. The combination of speed and low cost would allow comprehensive

range characterization to locate sources and movement of contaminants. Furthermore, it is important to note that while the system was tailored for perchlorate, this platform design can be modularized for the selective extraction and analysis of other low-abundance, military-unique contaminants from complex media.

1.2 Objectives

The ultimate goal of this project was construction of a novel LOC sensor to monitor perchlorate in ground and/or surface water in a sentinel mode with all the concomitant benefits of a remote, fieldable, inexpensive sensor. This proposal directly addressed the SERDP Environmental Research Statement of Need (ERSON) 09-02 for research leading to technology to detect and quantify perchlorate in groundwater on operational testing and training sites. In this limited-scope research project, we explored novel extraction chemistry designed to facilitate analysis of perchlorate in complex environmental media. This directly relates to and enables a tool for defining and understanding the environmental impact of munitions on operational ranges (DoD Directive 4715.11 and DoD Instruction 4715.14).

1.3 Approach

Specifically, this work studied novel selective and controllable surfactant-based extraction chemistry that can segregate and concentrate perchlorate from complex environmental waters. This affinity chemistry was combined with our current LOC sensor design to test our ability to embed this extraction scheme within sensitive and powerful microchip electrophoretic separations coupled to electrochemical detection, to create a new generation of sensors for low-abundance military contaminants.

We proposed to build on recent collaborative research performed in our laboratories on the analysis of perchlorate in surface water using microchip capillary electrophoresis (MCE). During preliminary studies completed on a related project, it was found that perchlorate could be resolved from interfering anions in less than 3 min, with detection limits at sub-parts-per-billion levels using direct injection of surface water. Tests using more complicated sample matrices such as wastewater proved more difficult due to the general increase in sample conductivity and high concentrations of interfering compounds such as chloride and nitrate. To meet the needs of real-world environmental monitoring at military ranges, new chemistry must be adapted that allows use of miniaturized MCE tech-

niques on more complex samples. We proposed a novel solution to this problem that integrates an extraction column for selective analyte binding by using zwitterionic surfactants in the first dimension and MCE in the second dimension. A zwitterionic, surfactant-coated, stationary phase would bind perchlorate while passing common anions such as chloride and nitrate. After sample extraction, perchlorate will be eluted from the phase by changing the pH or eluting the surfactant with organic solvent. Finally, although perchlorate is employed as the model in this work, the proposed system is based on platform technology that could be extended to monitor other munitions species of interest such as RDX, HMX, and TNT through the appropriate introduction of modules with desired specificity to create an integrated multi-analyte screening device.

The aim of this project was to develop a portable, inexpensive device for the detection of perchlorate in water at the parts-per-billion level. The developed device combines microchip capillary electrophoresis with zwitterionic surfactants that is capable of creating a miniaturized sorption zone which selectively and controllably binds and releases perchlorate in the presence of excess environmental anions. The final developed chip has selectively separated perchlorate from competing anions such as nitrate, chloride, and sulfate and has quantified perchlorate at the parts-per-billion level in drinking water.

2 Materials and Methods

2.1 Materials

All chemicals are reagent-grade unless otherwise stated. Silicon wafers (100-mm) were purchased from University Wafer (Boston, MA). Polydimethylsiloxane (PDMS) and Sylgard 184 elastomer were obtained from Dow Corning (San Diego, CA). SU-8 3025 photoresist and SU-8 developer was purchased from Microchem (Newton, MA). Sodium fluoride, 1,3-propane disulfonic acid disodium salt, and N-Tetradecyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (TDAPS), glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA), 1-dodecanol, cyclohexanol, and 2,2-dimethoxy-2-phenylacetophenone (DMPA), were purchased from Sigma-Aldrich (St. Louis, MO). Chloride, nitrate, and sulfate (potassium salt) were obtained from Fisher (Fair Lawn, NJ). Potassium perchlorate was obtained from J.T. Baker (Phillipsburg, NJ). Nicotinic acid was purchased from Fluka (Buchs, Switzerland). N-Hexadecyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (HDAPS) was obtained from Anatrace, Inc. (Maumee, OH). Tungsten microwires (13- μm diameter) were purchased from GoodFellow Corp. (Huntingdon, UK). Solutions were prepared in 18.2 M Ω water from a Millipore Milli-Q purification system (Billerica, MA).

2.2 Microchip fabrication

Construction of PDMS microchips was performed using previously reported methodologies with soft lithography (Duffy et al. 1998; Liu, Vickers, and Henry 2004; Noblitt et al. 2007). Briefly, a silicon wafer was spin-coated with SU-8 3025 at 800 rpm and prebaked at 65 °C for 3 min and 95 °C for 5 min. A mask was placed on the coated wafer and exposed to UV light for 7 s, polymerizing only the microchip features. Unpolymerized photoresist was removed in a bath of SU-8 developer, leaving only the channel mold on the wafer. Once the mold construction was completed and hard-baked at 80 °C overnight, PDMS pre-polymer was poured onto the mold and allowed to cure. Microchip fabrication was completed by removing the PDMS from the mold, inserting tungsten microwires, sealing the chip with a blank piece of PDMS by activating both surfaces with oxygen plasma. Copper wire leads were attached to the embedded microwires to interface with the external conductivity detector. Fabricated channels

were $50 \times 50 \mu\text{m}$ as determined by profilometry. Microwire spacing was $120 \mu\text{m}$, and the waste reservoir was 2 mm after the detection zone. The sample and buffer channels were 2 cm in length, the sample waste was 1.5 cm, and the separation channel was 5 cm. Microchips used in this study were fabricated with a bubble cell, and the design, fabrication, and optimization of the bubble cell were previously described (Noblitt and Henry 2008). A schematic of the microchip is shown in Figure 1.

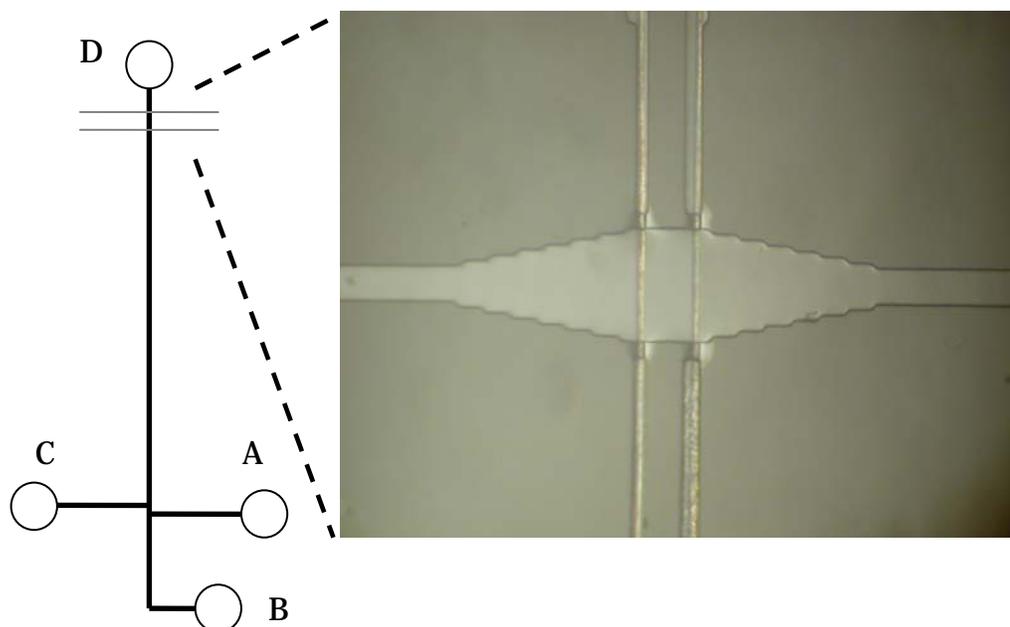


Figure 1. Microchip design shows that the bubble cell region is at the detection zone, seen as the expanded channel width in the photo (right), bisected by two tungsten microwires. Reservoirs are filled as follows: A = sample waste, B = sample, C = buffer, and D = waste.

2.3 Instrumentation and data acquisition

Contact conductivity detection was performed with a Dionex CD20 conductivity detector (Sunnyvale, CA) as described previously (Noblitt and Henry 2008). A National Instruments USB-6210 DAQ card and LabView 8.0 software (Austin, TX), running a custom Virtual Instrument, were used to monitor the output of the detector at a collection rate of 20 kHz with 2000-point boxcar averaging. No additional data filtration or smoothing was performed. A fifth-order, polynomial baseline fit was subtracted from the raw data to account for baseline drift resulting from reagent evaporation, ion depletion, and temperature fluctuations. A previously published, custom-built, floating high voltage power supply (HVPS) was used for electrophoresis (Garcia et al. 2003).

2.4 Electrophoresis

Separations on the microchip were performed in counter-EOF mode, in which the migration of analytes toward the detection zone is opposite the direction of electroosmotic flow (EOF; Yeung and Lucy 1998). Microchips were prepared by rinsing for approximately 30 s each with 18.2 M Ω -cm water and background electrolyte (BGE) consisting of 10 mM nicotinic acid and varying concentrations of surfactant. The zwitterionic surfactants, HDAPS and TDAPS, were used in the BGE system (Yeung and Lucy 1998; Okada 1997; Yokoyama et al. 2001). Gated injection was used throughout this study (Lacher et al. 2001; Jung et al. 2003). Each standard was made in 18.2 M Ω -cm water and mixed with 10% BGE to ensure conductivity consistency (Jung et al. 2003). An internal standard, 1,3-propane disulfonate (PDS), was used throughout this work to quantify perchlorate concentrations. Drinking water was collected from a potable water source in the Chemistry building at Colorado State University, Fort Collins, CO. Samples were prepared for electrophoresis by the addition of 10% BGE. For recovery studies, water samples were spiked with known concentrations of perchlorate.

2.5 Chromatography

Multiple perchlorate-surfactant binding studies were performed to explore the viability of a perchlorate extraction method based on electrostatic ion chromatography (EIC). A Metrohm USA, Inc. IC system (Riverview, FL) was employed with a C18 column coated with 30-mM TDAPS at a flow rate of 0.5 mL min⁻¹ for 5 h prior to the perchlorate studies. Three mobile phase compositions, which included varying concentrations of TDAPS, were tested to determine the ideal extraction parameters. Surface water samples were collected from the Cache la Poudre River in Fort Collins, CO. These samples were analyzed with the EIC system, with standard additions of known concentrations of perchlorate as sample pretreatment. Fractions of the eluted sample were collected following pretreatment, PDS was added, and the sample was analyzed with MCE to determine perchlorate recovery.

2.6 Monolith generation and perchlorate extraction

Single-channel microdevices were fabricated with soft lithography, as described in section 2.2, as substrates for monolith generation. A pre-polymer of the GMA-based monolith formulation was utilized, consisting

of GMA, EGDMA, cyclohexanol, 1-dodecanol, and DMPA in the amounts listed in Table 1 (Sun et al. 2008). The compounds were combined, sonicated for 10 min, then degassed with nitrogen gas prior to use. The single-channel devices were filled with the pre-polymer solution, utilizing a syringe pump at a rate of $10 \mu\text{L}\cdot\text{min}^{-1}$. Electrical tape was utilized to define the monolith within the channel. The monolith was polymerized in situ for 10 min under a 400-W UV lamp (Uvitron International, West Springfield, MA). After polymerization, the monolith was rinsed sequentially with 2-propanol and methanol to remove any remaining monomer and porogen from the channel. The monoliths were subsequently coated with 30 mM TDAPS prior to perchlorate studies at a flow rate of $50 \mu\text{L}\cdot\text{min}^{-1}$ for 1 h, which employed 1 mM TDAPS as the mobile phase.

Table 1. Formulation recipe for in situ-generated, GMA-based monoliths.

Compound	Weight (mg)
GMA	300
EGDMA	200
Cyclohexanol	150
1-Dodecanol	350
DMPA	25

3 Results and Discussion

3.1 Optimization of the MCE system

Several factors were considered when optimizing the MCE separation conditions, including buffer pH, field strength, injection time, and sulfobetaine surfactant composition and concentration. Nicotinic acid (10 mM) was chosen as the background electrolyte because of its relatively low pI (3.6) and its lack of electrochemically active, functional groups (Beckers and Bocek 2003; Persat, Chambers, and Santiago 2009; Persat, Suss, and Santiago 2009). Using an electrolyte with a low pH causes partial protonation of the silanol groups on the surface of PDMS, reducing the EOF within the channel. Additionally, low pH is integral in preventing interference by other anionic compounds in the sample. Compounds with pKa values greater than the buffer pH will be partially- or fully-protonated, slowing their migration toward the detector or preventing their detection entirely (see Section 3.3). The EOF of system was determined to be approximately $-1.2 \pm 0.5 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and was calculated from the migration time of the internal standard (Persat, Suss, and Santiago 2009).

The use of sulfobetaine surfactants was based on previous work which employed the ability of zwitterionic head groups to interact with the polarizable perchlorate ion (Lucy 2009; Mori et al. 2002; Yokoyama, Macka, and Haddad 2001). Sulfobetaine surfactants were used as BGE additives to improve the resolution of perchlorate from other anions. A series of electropherograms collected as a function of TDAPS surfactant concentration is shown in Figure 2. In the absence of surfactant, perchlorate was found to migrate more quickly than the internal standard, PDS. While perchlorate was resolved from chloride, nitrate, and sulfate in such separations, the resolution was deemed insufficient for environmental samples where the concentrations of these anions would exceed perchlorate by at least 1,000-fold. At concentrations above the critical micelle concentration (CMC), micelles of the surfactants can selectively interact with perchlorate, reducing its apparent mobility (Lucy 2009; Yokoyama, Macka, and Haddad 2001). Thus, the migration time of perchlorate was manipulated by varying surfactant concentration. Initially, HDAPS was tested because of its low CMC of $\sim 0.1 \text{ mM}$ (Yokoyama et al. 2001). HDAPS appeared to be

an excellent initial candidate for this separation; however, over time it was found to produce inconsistent migration times. Specifically, while the average retention time of perchlorate was 73 s, the relative standard deviation (RSD) was 48% (Figure 3). The cause of the instability is not understood at this point, but is likely due to the poor reproducibility of HDAPS adsorption to the PDMS channel (Garcia et al. 2005; Mora, Giacomelli, and Garcia 2007).

TDAPS was subsequently chosen as an alternative surfactant addition for the BGE. Similar to HDAPS, TDAPS was selected for its relatively low CMC of 0.4 mM (Yokoyama, Macka, and Haddad 2001). Perchlorate was effectively separated from chloride and nitrate, eluting after the internal standard when the TDAPS concentration was greater than 0.5 mM (Figure 2). The optimal concentration of TDAPS was determined to be 1.0 mM, based on peak resolution and shape. Employing this BGE system, a significant improvement in reproducibility was observed. The average retention time for perchlorate was 53.5 s with an RSD of 8.6%.

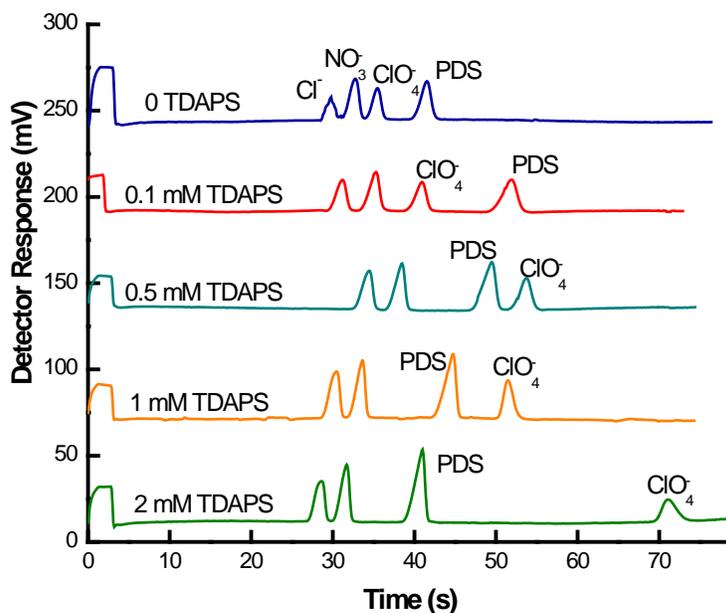


Figure 2. Electropherograms showing the changes in perchlorate retention with increasing TDAPS concentrations. Resolution for perchlorate and PDS is 1.87 ± 0.21 , 2.84 ± 0.19 , and 10.1 ± 0.23 when the TDAPS concentration is 0.5 mM, 1.0 mM, and 2.0 mM, respectively. Sample contains 5 μM analytes: 0.17 ppm chloride, 0.31 ppm nitrate, 0.50 ppm perchlorate, and 1.2 ppm PDS in 18.2 $\text{M}\Omega\text{-cm}$ water. Conditions: 10 mM nicotinic acid BGE, $-350 \text{ V}\cdot\text{cm}^{-1}$, 3.0 s injection. Detector range: 100 μS .

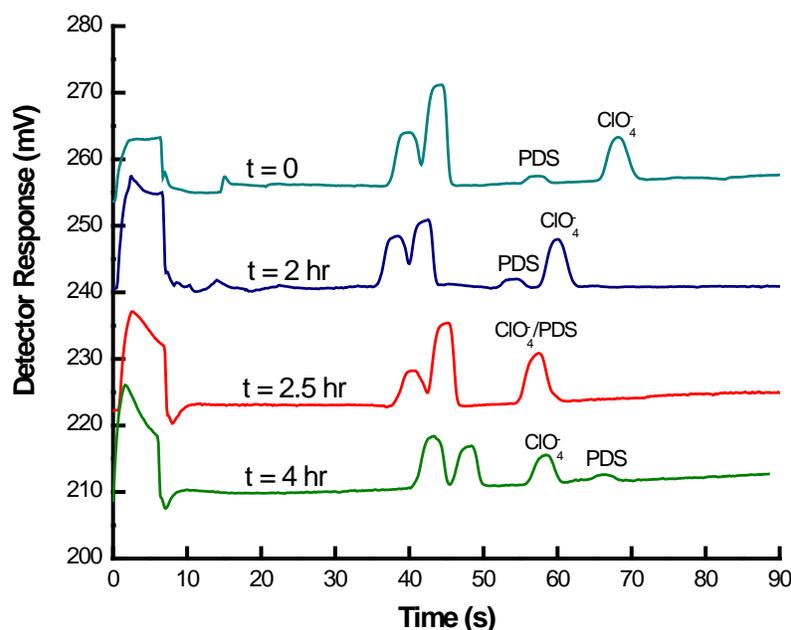


Figure 3. Electropherograms showing irreproducibility of the perchlorate retention time and the electroosmotic flow after 4 hr when HDAPS is used in the BGE. Conditions: 10 mM nicotinic acid, 0.5 mM HDAPS BGE, $-350 \text{ V}\cdot\text{cm}^{-1}$, 5.0 s injections. Detector range: 100 μS .

In addition to surfactant studies, field strength and injection time were also investigated. These parameters were optimized for both standards and drinking water samples. Initially, a field strength of $-200 \text{ V}\cdot\text{cm}^{-1}$ was used for optimizing surfactant concentrations; however, in later experiments, the field strength was increased to reduce analysis time. As shown in Figure 4, analysis time for standard samples was reduced as field strength was increased from $-200 \text{ V}\cdot\text{cm}^{-1}$ to $-500 \text{ V}\cdot\text{cm}^{-1}$. A significant increase in noise was observed at field strengths greater than $-400 \text{ V}\cdot\text{cm}^{-1}$, which detracted from the benefit of reduced analysis time. The optimal field strength was determined to be $-350 \text{ V}\cdot\text{cm}^{-1}$ and was used throughout the remainder of this work. Increasing the field strength from $-200 \text{ V}\cdot\text{cm}^{-1}$ to $-350 \text{ V}\cdot\text{cm}^{-1}$ reduced the analysis time from 100 s to approximately 60 s. Current IC techniques employed for perchlorate detection, in contrast, require run times of 15–30 min.

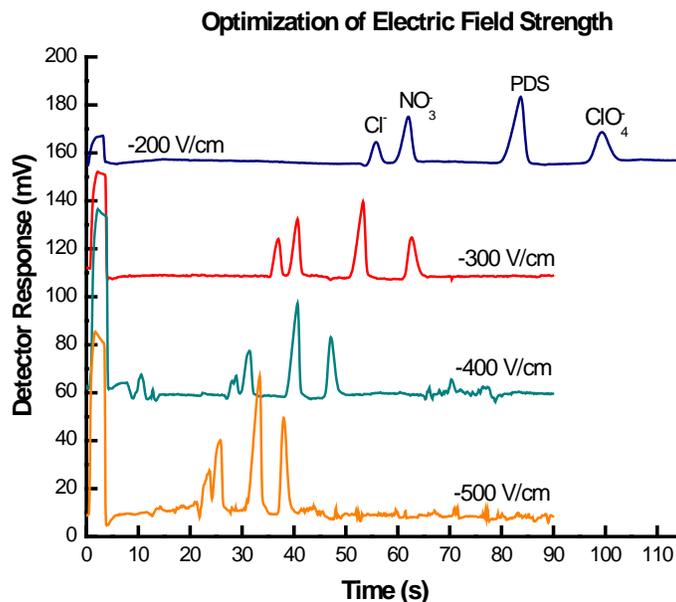


Figure 4. Electropherograms showing the changes in the separation with increasing field strength. Sample contains 5 μM analytes: 0.17 ppm chloride, 0.31 ppm nitrate, 0.50 ppm perchlorate, and 1.2 ppm PDS in 18.2 $\text{M}\Omega \cdot \text{cm}$ water. Conditions: 10 mM nicotinic acid, 1 mM TDAPS BGE, 3.0 s injection. Detector range: 100 μS .

Additionally, injection times were optimized to balance the amount of the sample injected during the gated injection with peak resolution. Since chloride and sulfate have the highest ion mobilities in water, more chloride and sulfate than other anions will be introduced into the microchip in a single injection (Figure 5). The large peaks generated from chloride, nitrate, and sulfate in higher ionic strength matrices, such as drinking water, were found to interfere with perchlorate analysis when injection times are long (greater than 10 s). Furthermore, peak shapes were compromised due to effects of a larger sample plug. The best injection time for standards ranged between 1 s and 5 s, while the optimal injection time for drinking water samples was determined to be 10 s.

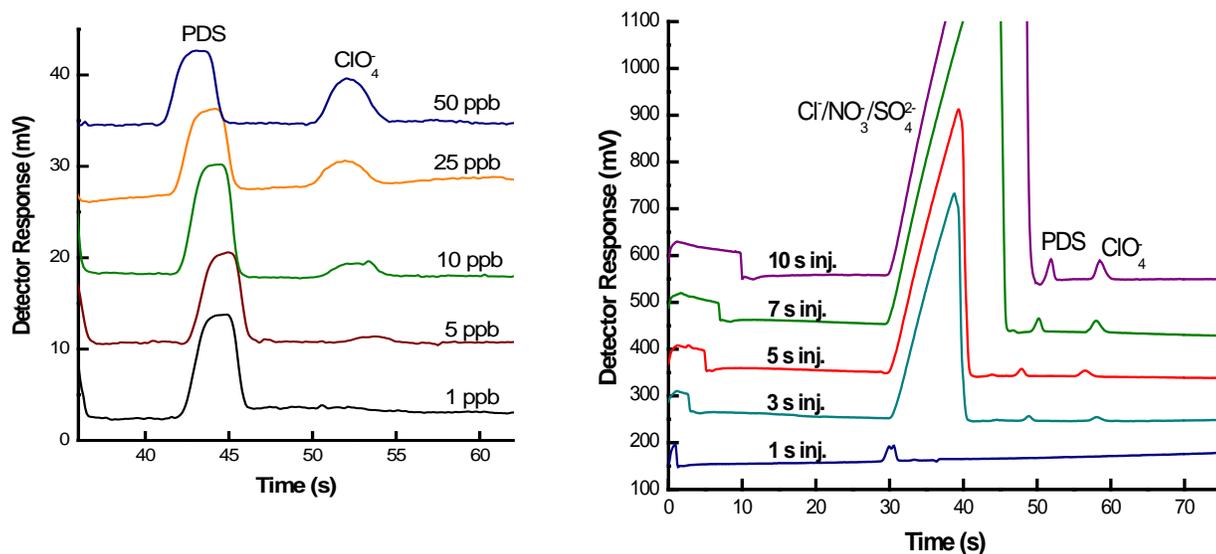


Figure 5.. Electropherograms showing the changes in peak areas with increasing injection time. Sample contains 100 ppb perchlorate and 0.124 ppm PDS in drinking water. The peak area for perchlorate increased from 11.4 mV s \pm 0.06, to 18.9 mV s \pm 0.02, to 34.9 mV s \pm 0.02, to 50.8 mV s \pm 0.08 for 3.0 s, 5.0 s, 7.0 s, and 10 s injections, respectively. Conditions: 10 mM nicotinic acid, 1 mM TDAPS BGE, -350 V \cdot cm⁻¹. Detector range: 100 μ S.

3.2 Limit of detection for perchlorate in standards

The LOD for perchlorate in standards was determined with the optimized separation conditions. Standards were prepared in 18.2 M Ω ·cm water and then diluted with 10% (v/v) BGE to provide consistent sample conductivity. The separation of PDS and perchlorate at concentrations between 1 ppb and 50 ppb is shown in Figure 6A. The LOD was 3.4 \pm 1.8 ppb for perchlorate (34 nM \pm 18 nM), S/N = 3. Additionally, perchlorate measurements were linear between 5 and 1000 ppb (R² = 0.9982, Figure 6B). The detection limit and linear range are within the USEPA's proposed health advisory limits and are comparable to that achieved by IC-CD systems.

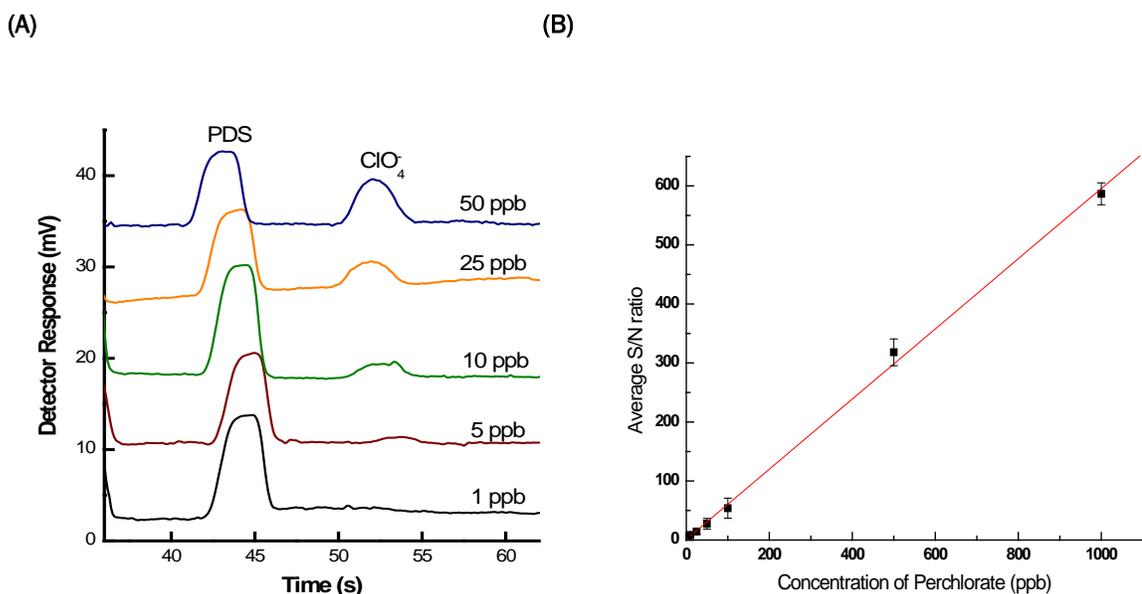


Figure 6. LOD studies of standard solutions with MCE. (A) Electropherograms showing the separation of perchlorate at concentrations between 1 ppb and 50 ppb. Electropherograms have been scaled to show internal standard and perchlorate peaks only. Sample contains 0.71 ppm chloride and 0.31 ppm nitrate, 0.12 ppm PDS, and 10% BGE (v/v) in $18.2 \text{ M}\Omega \cdot \text{cm}$ water. Conditions: $-350 \text{ V}\cdot\text{cm}^{-1}$, 3.0 s injections, BGE = 10 mM nicotinic acid, 1.0 mM TDAPS, pH 3.6. Detector range = $100 \mu\text{S}$. (B) Calibration curve plotting the change in average signal-to-noise ratio with increasing perchlorate concentration in standards. Linear regression: $y = 0.53133x + 1.2026$, $R^2 = 0.9982$.

3.3 Interferences

Possible interference from anions in drinking water was also investigated. Anions of greatest concern included chloride, nitrate, sulfate, and fluoride because of their ubiquity in drinking water. Early experiments proved the separation conditions capable of resolving perchlorate from sulfate, chloride, and nitrate, (and under the described conditions, fluoride) was not detected within a 120 s experimental window (Figure 7). Fluoride is not observed since the pKa value of the ion (3.17) is close to the pH of the buffer (3.6) which causes a substantial fraction of fluoride ions to be protonated, slowing its migration (Harrison, Sader, and Lucy 2006).

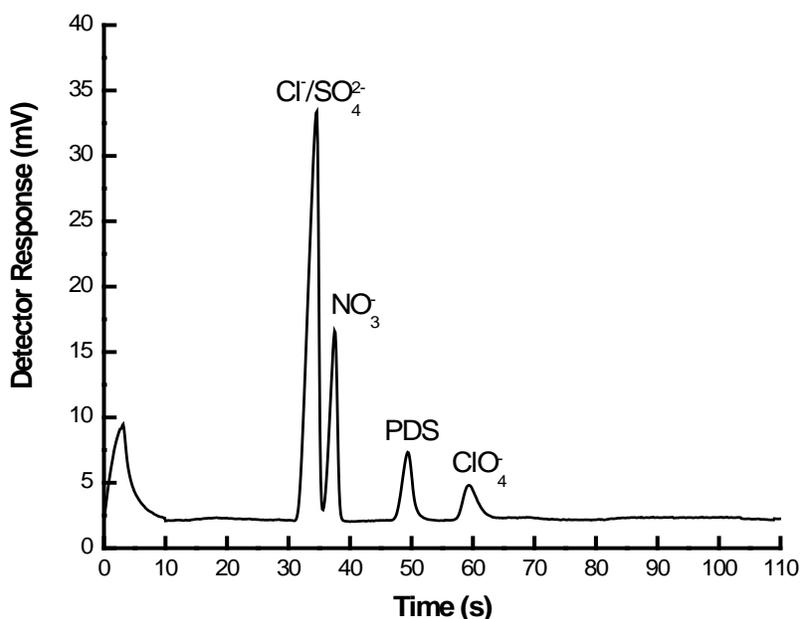


Figure 7. Separation of 1 μM analytes: 100 ppb perchlorate, 35.5 ppb chloride, 62.0 ppb nitrate, 135 ppb sulfate, 19.0 ppb fluoride, and 248 ppb PDS. Conditions: $-350 \text{ V}\cdot\text{cm}^{-1}$, 3 s injection, BGE = 10 mM nicotinic acid, 1.0 mM TDAPS, pH 3.6. Detector range = 100 μS .

3.4 Analysis of drinking water

Drinking water collected from the Colorado State University Chemistry building was analyzed for the presence of perchlorate. Though perchlorate was not detected in the native water sample, when the sample was spiked with 100 ppb perchlorate and 248 ppb PDS, both compounds were detected with 99% recovery for perchlorate, as calculated relative to PDS (Figure 8A). Thus, the microchip and separation conditions were capable of analyzing perchlorate in this environmental matrix. The LOD for perchlorate in drinking water was determined to be $5.6 \pm 1.7 \text{ ppb}$ ($56 \text{ nM} \pm 17 \text{ nM}$), $S/N = 3$, with the measurements linear between 10 and 1000 ppb ($R^2 = 0.9984$).

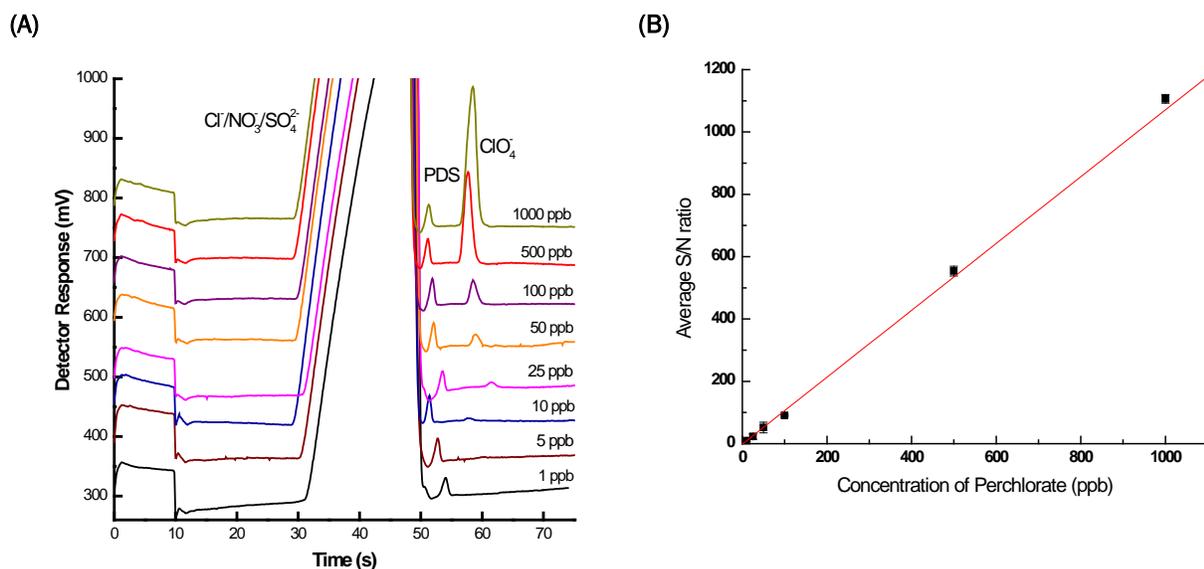


Figure 8. Analysis of perchlorate-spiked drinking water samples. (A) Electropherograms showing separation of drinking water samples spiked with 0.12 ppm PDS and concentrations of perchlorate between 1 and 1000 ppb. Conditions: $-350 \text{ V}\cdot\text{cm}^{-1}$, 10 s injection, BGE = 10 mM nicotinic acid, 1.0 mM TDAPS, pH 3.6. Detector range = $50 \mu\text{S}$. (B) Calibration curve plotting the change in average signal to noise ratio with increasing perchlorate concentration in drinking water. Linear regression: $y = 1.0645x - 3.0111$, $R^2 = 0.9984$.

3.5 Perchlorate extraction method

The experiments described thus far demonstrate the ability of the MCE method to analyze perchlorate at relevant concentrations in drinking water, an important accomplishment for improving drinking water quality. Broadening the applications of this device to analyze surface and ground water will aid in perchlorate remediation efforts and simplify the monitoring of perchlorate contamination in watersheds across the country as well as at US Army facilities. The large peak shown in Figure 8 was generated from relatively high concentrations of chloride, nitrate, and sulfate in drinking water, but this peak makes perchlorate detection difficult for the microchip system. This difficulty is exacerbated for higher ionic-strength matrices such as ground and surface water. To overcome this challenge, an extraction scheme that employs the fundamentals of EIC has been proposed. We expect the microchip performance to be improved by incorporating either a packed bed or monolithic channel that is coated with a zwitterionic surfactant acting as an extraction bed for perchlorate. The aim of this modification is to chromatographically separate perchlorate from high concentrations of chloride, nitrate, and sulfate prior to electrophoretic separation and subsequent conductivity detection. We have sought to model and optimize this extraction system using IC. Figure 9 shows the

separation of perchlorate from other anions using a commercial IC with a reverse-phase, C18 column that is coated with TDAPS.

By using the packed, extraction bed strategy, the effect of surfactant in the mobile phase on perchlorate retention was explored. De-ionized (DI) water, 0.1 mM TDAPS (below CMC), and 1.0 mM TDAPS (above CMC) were tested to determine how these different mobile phases affected perchlorate retention (Figure 10). Perchlorate retention was observed to shift to a longer retention time for mobile phases containing a higher concentration of TDAPS (1.0 mM) versus the lower concentration (0.1 mM) and DI water phases in which there was no micelle formation. Additionally, irreproducible perchlorate retention was observed when surfactant was present in the mobile phase in several studies. These phenomena are likely due to interactions between free surfactant in the mobile phase and the immobilized surfactant on the column. Since both an actual stationary phase (the TDAPS-coated C18 within the column) and a pseudostationary phase (micelles formed in the buffer) occur within this system, perchlorate is able to partition in and out of the moving micelles and with the TDAPS on the column, further slowing the migration of the anion through the column,

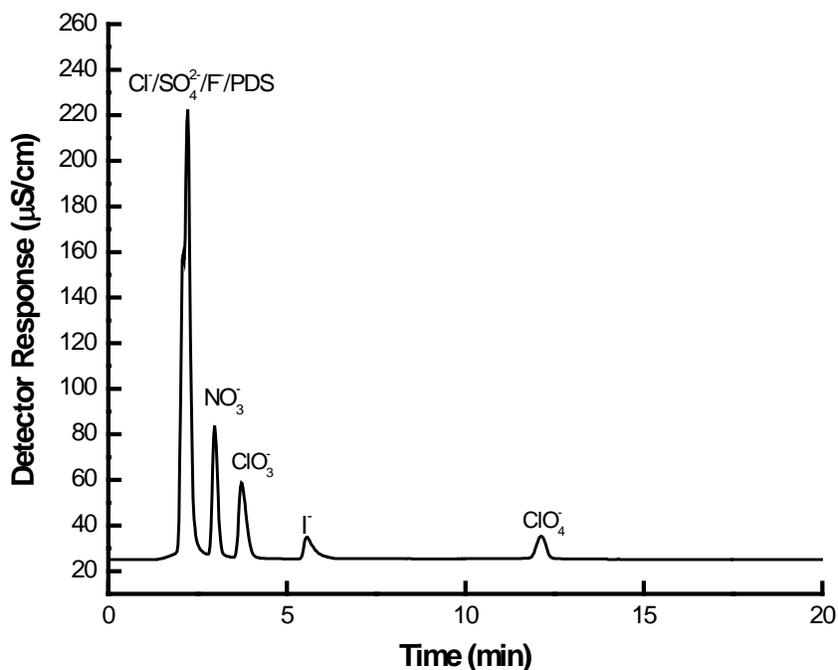


Figure 9. Separation of 1 mM chloride, nitrate, sulfate, fluoride, chlorate, PDS, and 0.5 mM perchlorate via EIC. Conditions: 1 mM TDAPS mobile phase, 20 µL injection volume, 10 mS_{cm}-1 detector range, 0.5 mL · min⁻¹ flow rate.

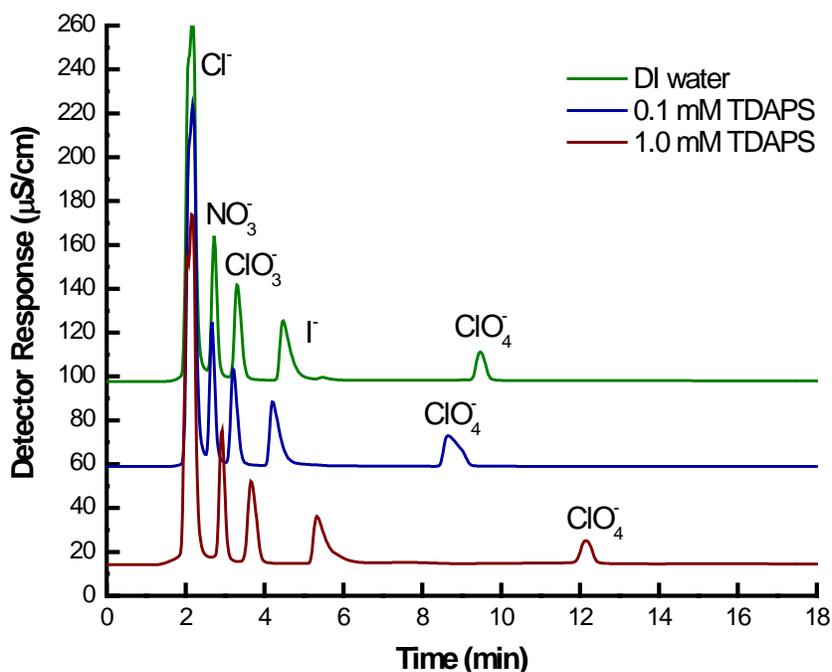


Figure 10. Chromatograms showing the change in perchlorate retention with increasing TDAPS concentration in the mobile phase. Sample contains 1.0 mM chloride, nitrate, chlorate, iodide, and 0.5 mM perchlorate. Conditions: 20 μL injection volume, 0.5 mL min^{-1} flow rate, 100 $\mu\text{S}\cdot\text{cm}^{-1}$ detector range.

when compared to separations having no micelles present. To improve reproducibility and keep the separation chemistry simple, DI water was utilized as the mobile phase after the column was pre-conditioned and equilibrated with TDAPS.

Unfortunately, a concentration threshold for perchlorate was also observed to occur on the column. At lower and more relevant concentrations, perchlorate is very strongly retained by the surfactant and does not elute from the column. Once the concentration threshold for the column is reached (a factor believed to be based on the number of available binding sites for perchlorate on the immobilized surfactant), the excess perchlorate is eluted and reaches the detector. While this effect has been problematic for the detection of perchlorate at the parts-per-billion level with the present EIC system, the extraction method has been used to successfully separate and detect perchlorate in a surface water sample.

A surface water sample was collected from the Cache la Poudre River in Fort Collins, CO. With no sample pretreatment, the water was spiked with 100 μM perchlorate and injected onto the reverse-phase column. The exact concentrations of competing anions are not known; however, these con-

concentrations were high enough to overload the conductivity detector on the IC and certainly too high for analysis via MCE (Figure 11A). Once perchlorate was separated from these anions and detected, the perchlorate peak was collected in a 0.5 mL fraction. This fraction was spiked with 0.5 μM PDS for quantitative purposes and 10% BGE for EOF stability, and then analyzed by MCE. By extracting perchlorate from a high ionic-strength sample matrix, analysis via MCE is possible. As shown in Figure 11B, the concentration of competing anions was drastically reduced following EIC pretreatment. The concentration of perchlorate in the fraction, calculated relative to PDS peak area, was 133 ± 11 ppb, a recovery of only 1.3%. The low-percentage recovery is most likely due to the concentration threshold that exists for perchlorate on the IC column. A large fraction of the injected perchlorate is irretrievably lost on TDAPS binding sites in the column. Possible solutions to this problem are discussed in Section 4 that discusses conclusions and implications for future work.

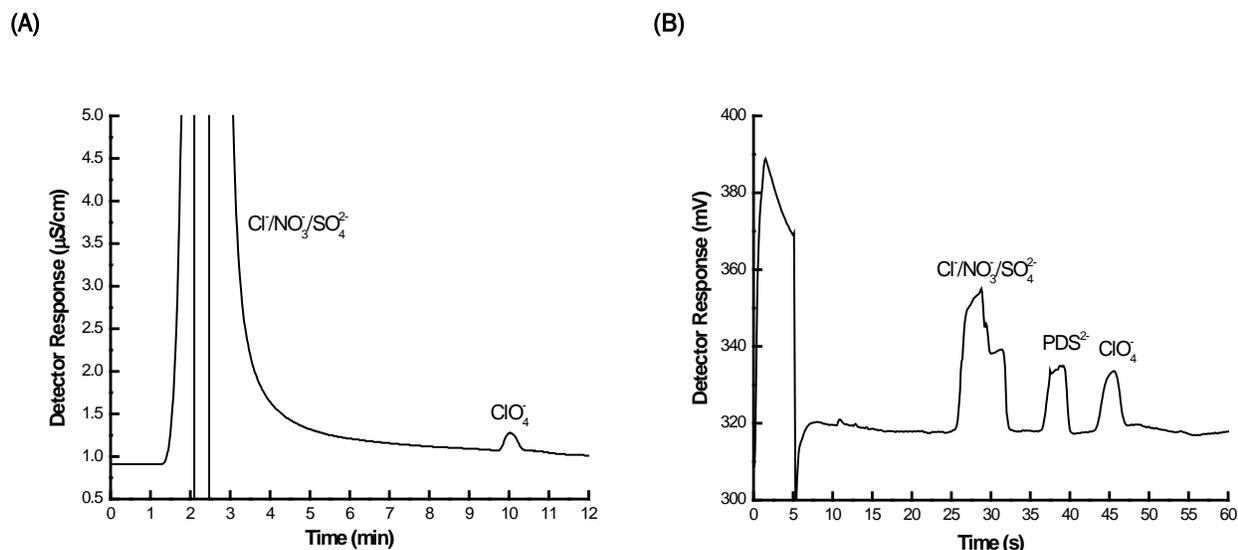


Figure 11. Analysis of surface water from the Cache la Poudre River. (A) Chromatogram showing the separation of 100 μM perchlorate from competing ions in the surface water sample. Conditions: 100 μL injection volume, 0.5 mL $\cdot\text{min}^{-1}$ flow rate, 100 $\mu\text{S}\cdot\text{cm}^{-1}$ detector range. (B) Electropherogram showing the separation of perchlorate, collected as an eluted fraction from the IC column. Conditions: $-350\text{ V}\cdot\text{cm}^{-1}$, 5.0 s gated injection, BGE: 10 mM nicotinic acid, 1.0 mM TDAPS, 50 μS detector range.

In efforts to integrate these preliminary studies on a chip format, analogous stationary-phase monoliths were generated in situ in single PDMS channels. These single channels were 2-mm wide by 2-cm long to maximize the area available for perchlorate to interact with the coated monolith

and included a bubble cell for conductivity detection similar to that for the MCE devices (Figure 12). To generate the GMA-based monoliths, a prepolymer solution was introduced and photopolymerized in defined areas of the channel, leaving the bubble cell containing the tungsten microwires clear for detection. Preliminary experiments were completed to determine the how well perchlorate was retained on monoliths coated with TDAPS surfactant. As shown in Figure 13, the plug of perchlorate injected into the channel displayed similar elution profiles across chromatograms with average retention times of 24.4 s (RSD = 20.0 %) and 8.7 s (RSD = 16.3 %) for the 100 $\mu\text{L}\cdot\text{min}^{-1}$ and 250 $\mu\text{L}\cdot\text{min}^{-1}$ flow rates, respectively. The short retention times indicate that although the perchlorate is interacting with the surfactant present in the 1 mM TDAPS mobile phase, there appears to be no interaction between the perchlorate and the TDAPS coating of the monolith. This phenomenon is likely due to the lack of surfactant binding to the monolith. Initially, it was expected that the surfactant would physisorb to the monolith as it did to the C18 packing of the IC column since the exposed epoxide functional groups of the monolith are uncharged. The compact and polarizable nature of these moieties, however, clearly affects the sorption of the zwitterionic surfactant which includes an alkane chain that permits the surfactant's interaction with the long alkane chains found on the reverse-phase IC column used in the packed bed experiments. Modifications to the monolith formulation to resolve this issue are discussed in Section 4.

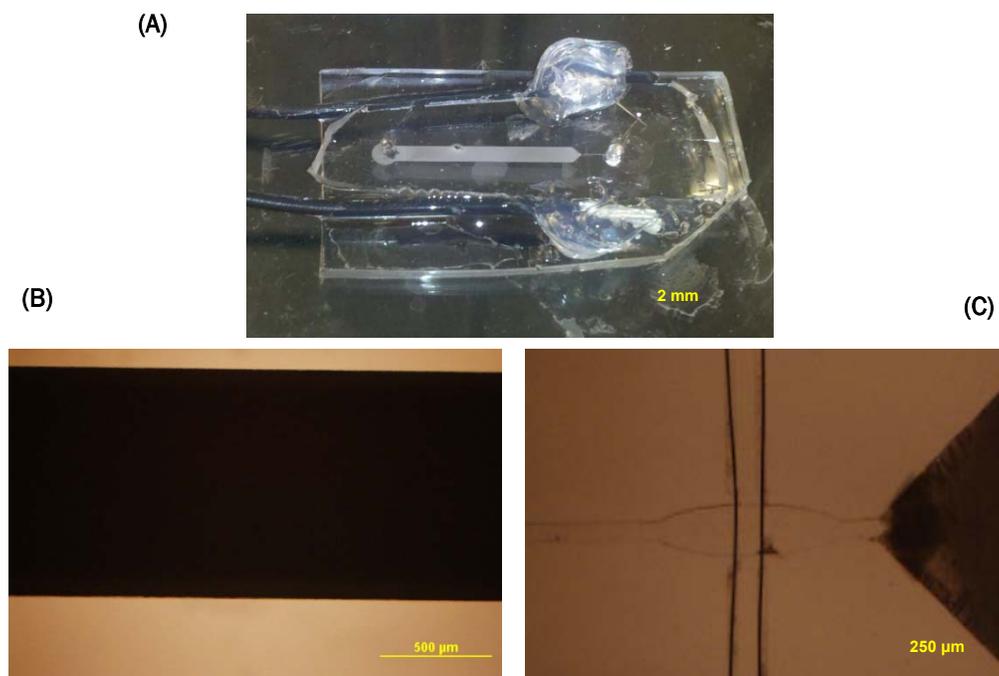


Figure 12. Monolithic channel with detection bubble cell. Channel was 2 mm wide, 20 mm long, and 50 μm high. (A) Complete device with copper wire external electrode connections (black wires), (B) magnification of middle portion of the channel detailing complete monolith coverage throughout the channel, (C) magnification of the detection bubble cell with the tungsten microwires.

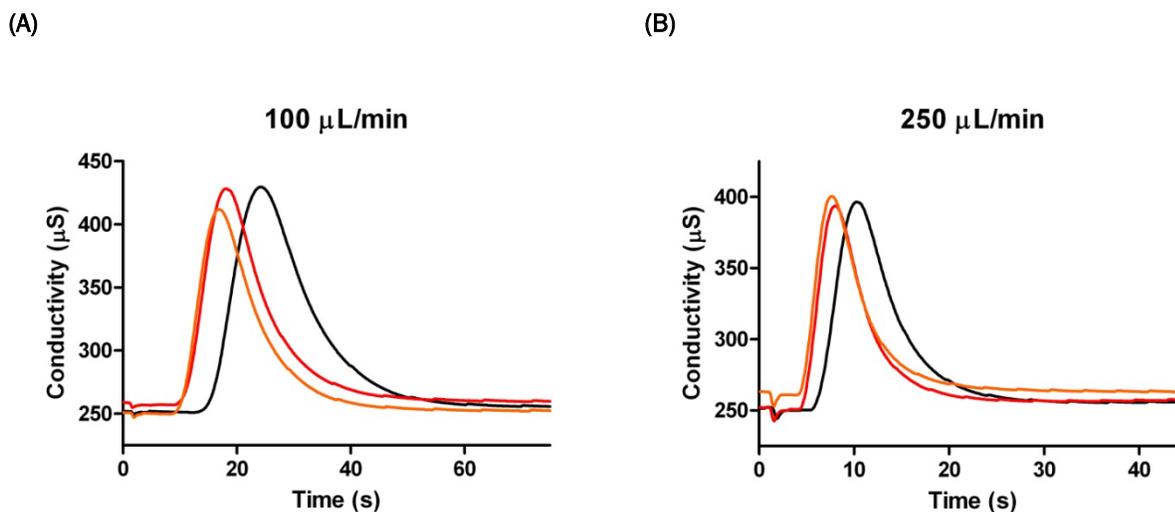


Figure 13. Chromatograms showing the retention of 1 μM perchlorate at 100 μL·min⁻¹ (A) and 250 μL·min⁻¹ (B) flow rates with injection volume of 4.2 μL. Each line in the graphs represents a replicate separation performed on the same monolith. Short migration times of perchlorate (less than 50 s) indicate that no appreciable TDAPS has been coated onto the monolith and the retention of the ion is due only to the surfactant present in the mobile phase.

4 Conclusions and Implications for Future Work

An MCE device has been developed for the detection of perchlorate in drinking water samples. Separation chemistry has been optimized, including the comparison of two zwitterionic sulfobetaine surfactants. The device is capable of analyzing perchlorate over a relatively large linear range, with a detection limit of 5 ppb in drinking water that satisfies the USEPA regulatory requirement. Additionally, analysis times for the method are approximately 15–30 times shorter than current IC techniques. This work was recently published in *Analytical Chemistry* (Gertsch et al. 2010).

To broaden the device applications, we have investigated an on-chip extraction method to selectively concentrate perchlorate from higher concentrations of competing anions that are present in ground and surface water. Ultimately, the extraction will take place directly prior to electrophoretic separation, enhancing the device's abilities to analyze higher ionic strength matrices. The extraction method is based on EIC in which a zwitterionic surfactant is immobilized on either a packed C18 column or monolith and a simple mobile phase, such as water, is used to elute analytes. We have explored both platforms and demonstrated proof-of-concept by extracting perchlorate from a surface water sample, which was then analyzed via MCE. Without this extraction step, the surface water sample could not have been directly injected into the microchip due to the high background conductivity. Issues with the concentration threshold of the packed bed platform could benefit from the use of a dilute electrolyte solution as the mobile phase to help equilibrate and stabilize the binding sites of the TDAPS coating. Additionally, problems with the surfactant coating of the monolith surface could be ameliorated by chemically modifying the epoxide moieties of the exposed functional groups to generate a more useful, permanent, and stable interaction between the functional groups and TDAPS.

While the method still faces some challenges, the ability to significantly reduce the concentration of competing anions in surface and ground water shows great promise for the device as a fieldable tool for perchlorate remediation sites and US Army facilities.

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Appendix A: List of Publications from Project ER-1706

1. Articles in peer-reviewed publications:

Gertsch, J. C., S. D. Noblitt, D. M. Cropek, and C.S. Henry. 2010. "Sub-ppb Detection of Perchlorate Using Microchip Electrophoresis." *Analytical Chemistry* 82: 3426–3429.

2. Conference or symposium abstracts:

Henry, Charles, Jana Gertsch, and Donald Cropek. 2010. "On-Line Perchlorate Monitoring by Microchip Electrophoresis" presented at Pittcon 2010 in Orlando, FL.

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14. ABSTRACT Perchlorate is a pervasive water contaminant that has drawn national attention as a public health concern. Although perchlorate contamination has both natural and anthropogenic origins, its recurrent use in military munitions makes perchlorate the highest-priority military pollutant. Currently, perchlorate detection at the critical parts-per-billion level requires large, sophisticated instrumentation in a centralized laboratory. This report describes a fieldable, microchip capillary electrophoresis (MCE) device that is selective for perchlorate and exhibits reduced analysis times and reagent consumption. The device employs contact conductivity detection and zwitterionic surfactant chemistry to selectively resolve perchlorate from abundant environmental species such as chloride, nitrate, and sulfate. The prototype MCE system is capable of detection limits of 3.4 ± 1.8 ppb in standards and 5.6 ± 1.7 ppb in drinking water. Additional work modified the microchip geometry and separation chemistry, to account for higher ionic strength sample matrices such as surface and ground water, which cause interferences with perchlorate detection. A novel extraction method, incorporating the fundamentals of electrostatic ion chromatography (EIC), is presented as a way to overcome this challenge. Two extraction formats, employing either a packed bed or a monolith, were also investigated and presented in this work.					
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