



WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Development of a Ground-based Water Analyzer for Remote Sensing of Nitrates and Phosphates in Surface Water

Focus Categories: NC, NPP, WQL

Keywords: Water Quality Monitoring, Non-Point-Source Pollution, Remote Sensing, Nutrients, Nitrates, Phosphates, Fertilizers, Runoff

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Congressional District: Third

Statement of Critical Regional Water Problems:

There exists a critical need for a better understanding of nonpoint source (NPS) pollution. NPS pollution consists of any material that can adversely effect surface or ground water (including aquifers). NPS pollution is usually generated from diffuse sources in short bursts associated with events such as rainfall. These NPS pollutants can be categorized as acids and salts, sediment, nutrients, heavy metals, toxic chemicals and pathogens. Of special importance to the citizens of Mississippi, is nutrient-based NPS pollution. Mississippi has a strong agricultural base in cotton, soybean and rice production, all requiring extensive use of fertilizer to enhance production. Runoff during a rain event can lead to NPS pollution in the form of nitrogen, phosphate, and potassium. Of these, the nitrogen sources, ammonium, nitrate, nitrite, and organic nitrogen are keenly important. Other major Mississippi agricultural operations, poultry and swine production, are also large generators of nitrogen based nutrients. Nutrients leached from these agricultural operations can increase algae and other aquatic plant growth rates in surface waters. Along with sediments, this can lead to increased rates of eutrophication. Certain of these nutrients, nitrites and nitrates, are regulated to less than 10 ppm in drinking water, therefore of special concern regarding infiltration into ground waters.

A major problem in regulating NPS pollution is the time required to sample and analyze a temporal event. Typically, surface or ground water samples are taken in the field and transported to a laboratory for analysis. The water samples are analyzed by ion chromatography. The data are processed, a report is generated and communicated to the

submitter. This process can take several days to as long as a week. The event has passed, it is impossible to resample or to take additional samples. If the evolution of a NPS pollution event could be monitored by a fast analytical approach, then proactive steps could be taken to remediate the damage as the event is unfolding.

Statement of the Results, Benefits, and/or Information Expected

The primary goal of this proposed effort is to construct a prototype microfabricated ground-based water analyzer (GBWA) capable of providing remote and real-time monitoring of water chemistry. In particular, methods for the monitoring of nitrates and phosphates will be developed due to their importance to water quality and connection with agricultural NPS pollution. These pollutants are of particular concern in rural, agricultural areas where remote sensing by satellite would be especially useful. The basic idea is to develop a compact and self-contained chip-based analytical device which would automatically and periodically analyze for nitrate and phosphate using capillary electrophoresis. Each unit would be equipped with a radio transmitter capable of relaying the analytical data either directly or indirectly to a satellite for remote sensing of the ground-based measurements. The data could be relayed either to a central site or to a distributed computer network for effective water management.

The output of these nutrient analyzers could be correlated to satellite data greatly advancing our knowledge regarding NPS pollution. This enhanced data set could be used to modify the “best management practices” of Mississippi agriculture greatly improving the utilization of nutrient resources. Additionally, this would allow convenient access to chemical movement data which could also be correlated with other Geographic Information System (GIS) data such as rainfall events, land use, etc. The increased spatial and temporal resolution of measurements could potentially in some cases locate the primary source of NPS pollution. It is expected that analyzer units would be inexpensively deployed in the field and remain unattended for an extended period of time.

Nature, Scope, and Objectives of the Research

Effective environmental monitoring typically suffers from sampling difficulty due to labor intensive manual sampling resulting in poor data resolution in both temporal and spatial dimensions. This project proposes to demonstrate a proof of concept for rapid, ground-based chemical analyses with remote data retrieval provided by satellite relay. Depending on the application, the specific analytes could easily vary from those selected for this initial prototype. One could imagine deployment of various types of chemical analyzers to cover a wide range of analytes with real-time remote sensing capabilities and the concomitant ability to correlate the chemical data with other satellite data.

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source (NPS) pollution. These pollutants are of particular concern in rural, agricultural areas where remote sensing by satellite would be especially useful. The basic idea is to develop a compact and self-contained chip-based analytical device which would periodically analyze for nitrate and phosphate using capillary electrophoresis. Each unit would be equipped with a radio transmitter capable of relaying the analytical data indirectly to a satellite for remote sensing of the ground-based measurement. This would allow convenient access to chemical movement data for correlation with other Geographic Information System (GIS) data. It is expected that analyzer units would be deployed in the field and remain unattended for an extended period of time.

The most common method for the detection and quantification of small inorganic ions is ion chromatography. Capillary electrophoresis (CE) is also capable of rapid analysis of inorganic ions and requires less sample and less sophisticated instrumentation than LC. The primary limitation to the use of CE is the poor sensitivity of most detection methods (typically optical) for small inorganic ions. Ion chromatography typically relies upon conductivity detection, which until very recently, was not available on commercial CE systems. Microchip CE holds great promise for rapid separation and quantification of complex analyte systems with little or no sample preparation. Additionally, the small size and power requirements of these systems provide great potential for remote separation-based sensing applications.

A remote sensing system for analysis of nitrites, nitrates, and phosphates based on microchip CE will require the demonstration of the following developments: 1) microchip CE conductivity detection, 2) microchip CE separation of small inorganic ions, 3) on-chip sample filtration and preparation, and 4) integrated sampling.

Methods, Procedures, and Facilities

The development of a microfabricated device for real-time monitoring of NPS surface water contamination requires an integrated approach. The construction of the devices, often called total analysis systems (TAS), use simplified electrical engineering techniques.¹⁻⁵ Once the devices are constructed, the determination of contaminants in this project relies on direct sampling with integrated capillary electrophoresis and conductivity detection. During this phase of the project, only the microfabricated capillary electrophoresis and conductivity detection parts will be developed.

For this prototype work, the design (Figure 1) consists of a single separation channel, a sample introduction channel, and several electrodes for conductivity measurements. The design consists of two basic layers which are fabricated independently and then combined to produce the final product. One layer is constructed in elastomer using injection-molding (Figure 2). This layer contains the separation capillary (~75 μ m wide by 40 μ m deep), buffer and sample reservoirs, and the sample introduction capillary. The second layer supports the electrodes for driving the separation and for the conductivity measurements. Two forms of conductivity detection will be evaluated in this project. The first is direct contact conductivity where the electrodes are exposed to solution and the change in resistance between two electrodes is measured.⁶⁻⁸ The second is non-contact

conductivity where the electrodes are covered with a thin layer of non-conducting material and the change in resistance is measured between two electrodes.⁹⁻¹¹ The first system is easier to construct, however the exposure of the electrodes to the solution may create problems with biofouling and require the use of the second system.

The fabrication of an injection-molding master is relatively straightforward (Figure 2). This method is selected because it requires a minimal amount of fabrication time and the production of numerous capillary channels is possible once the master has been constructed.^{1-3,5} First, a silicon wafer is spin-coated with a special epoxy that is UV sensitive. This must be done in a clean-room; a well-controlled environment that has minimal UV light and is ultra-clean. These facilities exist at MSU in the department of electrical engineering. The construction of such a facility within the chemistry department has begun as well. Once the wafer is coated with epoxy, a special glass plate, called a mask, containing the desired pattern is placed on top of the wafer. Commercially produced masks are expensive (\$500-\$1000 each). We will use relatively new rapid prototyping during this phase of the project where the masks are made using an overhead transparency.¹ The sandwich is then exposed to intense UV light for a short period of time. The wafer is rinsed in a developing solution, leaving behind only the unexposed epoxy. This material is cured in an oven at 65°C for one hour. The completed master has an expected lifetime of 100 moldings and can be used until it either breaks (the most common cause of early demise), the epoxy is pulled off, or the design requirements change.

The second phase of microfabrication is the construction of the electrode plate. The electrodes can be constructed on various materials ranging from plastics to glass. For this prototype system, glass squares (3") will be used. The first phase is to coat the glass with electrode material. For the electrode system to be rugged, either gold or platinum must be used. The coating is very thin (150 nm or <0.00001") resulting in a low cost-per-chip even with the use of these precious materials. For the prototype design, gold will be used. A layer of UV-sensitive polymer is placed on the gold-coated glass square. A second mask containing the electrode pattern is placed on top of the square and the sandwich exposed to intense UV light. The exposed polymer is then removed in a developing solution. The exposed gold is etched. Once this gold has been etched, the protective polymer layer is removed in a separate solution leaving behind a pattern of gold electrodes. The prototype design will contain four detection electrodes. This repetition in design allows the use of alternative electrode systems if one of the electrodes should fail and does not add to the cost of construction. If the lifetime of the electrodes becomes an issue, a larger number of electrodes may be fabricated in

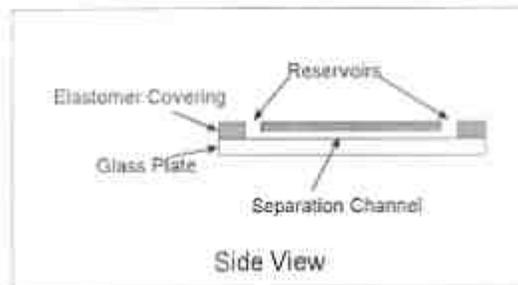
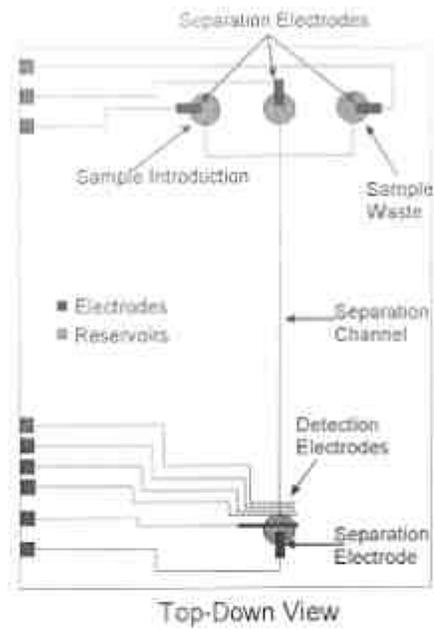


Figure 1: Top-Down and Side View Schematics of a microfabricated system for remote sensing of non-point source contamination.

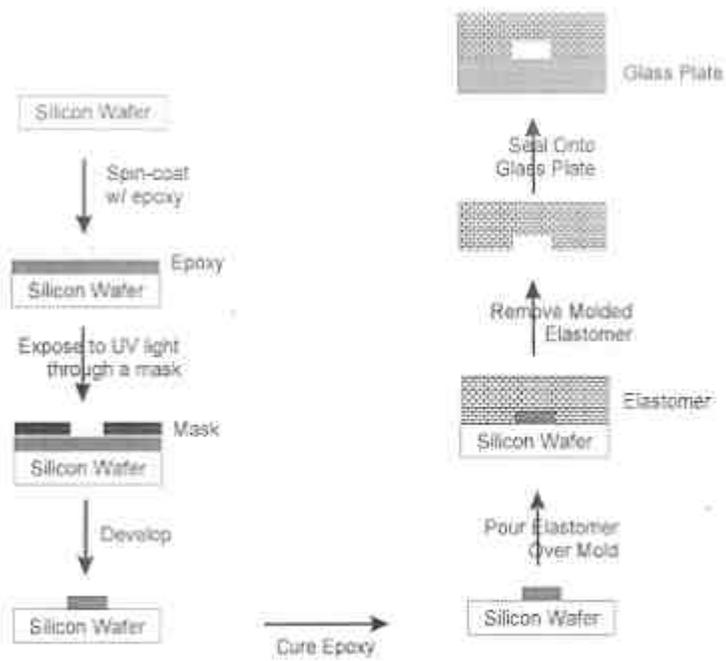


Figure 2: A schematic of the injection-molding process from fabrication of the molding master through the molding process.

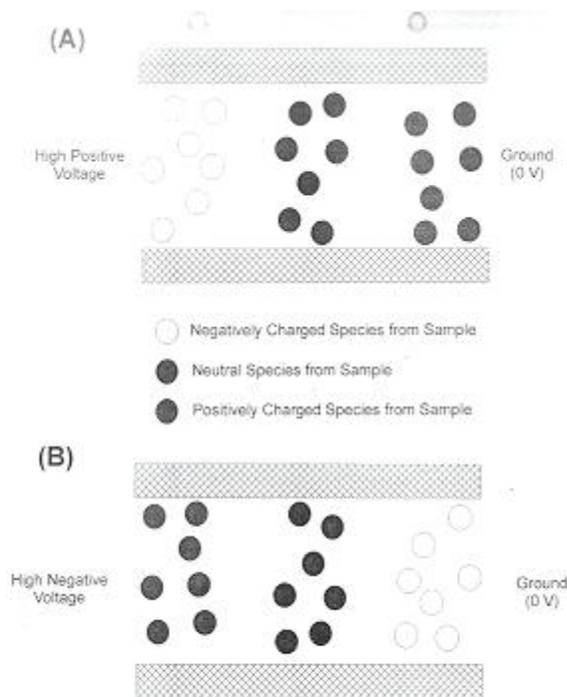


Figure 3. Schematic drawing of the separation process for capillary electrophoresis under high positive applied voltage (A) and high negative applied voltage (B).

close proximity to each other to further increase system longevity. For direct contact conductivity detection, this is the end point of the electrode plate fabrication. Non-contact detection requires the addition of a thin insulator on top of the electrodes. Two methods will be evaluated, if this step is necessary. The first is to coat the glass square after fabrication of the electrodes with a thin ($1 \frac{1}{4}\mu\text{m}$) layer of SiO_2 . This is done using plasma-enhanced chemical vapor deposition (PECVD). The SiO_2 is patterned so that the contact pads and the separation electrodes are exposed while the detection electrodes remain covered. Alternatively, the electrodes will be coated with a thin polymer layer. The polymer can be patterned by exposure to intense UV light through a mask and cover only the detection electrodes.

Once the individual components have been constructed, the TAS must be assembled. Immediately prior to assembly, both components are cleaned, first by extensive rinsing with isopropanol, then in an inexpensive oxygen plasma cleaning system. This insures reproducibility of flow and a permanent seal once the layers are combined. The separation channel is aligned so that the electrodes used for detection and quantification of the system are located at the end of the separation channel. The electrodes used for driving the separation and for introducing the sample into the separation channel are aligned in their respective reservoirs. The alignment is done under a low power microscope with a calibrated eye piece to ensure consistency of alignment.

The separation of common anion contaminants will be accomplished using capillary electrophoresis (CE). CE separates analytes based on size, ionic charge, and polarity (Figure 3). The order of migration for the species will be pH and voltage dependent, but is predictable. At pH 7, the order of migration will be nitrite, nitrate, and phosphate under negative potential control. At pH 10, the order of migration will be phosphate, nitrite, and nitrate. The shift in the migration order as a function of pH will need to be optimized to realize the fastest separation while still maintaining resolution of the contaminant species. The polarity of the voltage will also affect the separation. Under standard capillary electrophoresis conditions using a positive voltage field, the anions will not travel through the capillary. Two approaches will be investigated. The simplest method is to reverse the field polarity, making it negative.^{9, 10, 12, 13} One concern with this approach is the time required for the separation. A second approach is to modify the capillary wall with a thin layer of material to reverse the flow. This has shown the fastest separation times, however it adds complexity to the analysis and instrumental setup.¹⁴⁻¹⁶ The field strength (volts/cm) required to separate these species must also be studied. Ideally, the faster the separation, the lower the total power consumption of the system as the electronics would be on for shorter periods of time. To increase the separation speed, we must increase the field strength. Typical CE separations use ~200 V/cm. With the microfabricated systems we can if needed, increase this to two to three times this value. Analysis times of less than 30 sec. are expected.

Sample loading and separation in the microfabricated systems can be automated. The sample will be introduced through the intersection of the sample and separation channels by applying a voltage between the sample and sample waste reservoirs (Figure 1). Typically this field is 100 V/cm. The separation proceeds by applying a voltage between the buffer inlet and outlet of the separation channel (Figure 1). The initial prototype design contains a 5 cm separation channel and therefore would require 1,000 V between the reservoirs to generate a field strength of 200 V/cm. Although a high voltage is used, the current is low (1–¼A range) allowing long lifetimes from a battery. Simple electronics allow the voltage to be switched between the sample introduction and separation reservoirs and thus will allow for rapid automatic and repetitive analysis, if needed.

The primary issue during the separation is the isolation of the signal from the anions in the sample from that of the buffer system. This may be accomplished by selecting a buffer system that has a substantially lower conductance than the contaminate anions. The best separation will be accomplished using an amphiphilic buffer system such as N-tris-[hydroxymethyl]-methyl-2-aminoethanesulfonic acid (TES). It should be noted that the separation of both anions and cations in a single run is difficult as they move in opposite directions under the influence of a single voltage field polarity.¹⁶ This is not a problem as the TAS can be constructed with two separation channels, one for anions and one for cations. Therefore, a similar analytical approach could be applied to the detection of cations such as potassium in the future.

Detection Methods for the Water Analyzer

The detection method to be developed and used in the ground-based water analyzer (GBWA) is based on electrical conductivity. As the zones of separated analytes (i.e. nitrate and phosphate ions) migrate through the CE channel of the GBWA, the conductivity of the background electrolyte (BGE) will change as a consequence of the different ionic mobility of the analyte and BGE ions.^{17,18} In the device described here, the separated analyte zones will contain ions with higher ionic mobility than that of the BGE and thus the conductivity in these zones will increase above the background. Placing a suitable detector at the end of the CE separation channel will allow detection and quantitation of the ion concentration in the separation zones.

Detectors for any separation method are chosen for their sensitivity, selectivity, and precision. In addition, the detector and associated electronics used in this device must be physically small and rugged and have low power requirements. In these regards, the conductivity detector is nearly ideal. Conductivity detection is well-established as a “universal” detector for liquid chromatography¹⁹ and has now been employed as a detector for numerous CE experiments.¹⁷ As a universal detector, conductivity can be used to detect the presence of any ionic or nonionic species, the later by a decrease in conductivity, provided the analyte and BGE have sufficiently different ionic mobility. Since there are a large variety of choices of BGEs, almost no situations arise in which mobility differences are not available. The detection limit of the conductivity detector under conditions similar to those proposed here is about 2×10^{-6} M (mol/liter)²⁰, which is sufficiently sensitive to detect 100 parts-per-billion nitrate in the GBWA..

Other possible choices for detection were rejected because they add an unacceptable complexity to the experiment.¹⁸ Optical methods, such as ultraviolet (UV) adsorption or fluorescence, are popular methods for use in CE and liquid chromatography (LC) applications; however, this application would require development of rugged, miniaturized, low-power optical accessories, such as lenses, lamps, and photo-detectors. Mass spectrometric detection is excluded due to the lack of miniature equipment. Electrochemical, EC, detection is a potential future detection method for use in the GBWA. EC detection is similar to conductivity in its ability to be miniaturized and it is a more sensitive method.⁸ Drawbacks to EC detection are the increased susceptibility to detector fouling and a lack of universal detection for inorganic ions.

Because there is no commercial conductivity detector (CD) designed for use in miniaturized CE systems, a significant effort is required in the development of this device. The conductivity detector uses the ac conductivity of the BGE and the analyte zones. The two types of methods to be explored are known as “contact” (end- or in-column) and “contact-less” CD (described below). Each method has advantages and choosing the most suitable method is a goal of this work. As part of this goal, the detection-limit and linear dynamic range for concentration measurement of nitrate and phosphate ions will be determined. In addition, the long-term stability of the detector is a critical design feature. Predictable response over a one-week period is a minimum goal and stability over that time frame will be investigated. As part of this investigation, the

detector will be challenged by introducing likely interferents (e.g. humic acid) and any change in response will be noted. An advantage to the CD is that the baseline conductivity of the BGE can be used as a control. Significant drift or deviation of the measured BGE conductivity indicates a stability problem. Investigation will determine if the BGE conductivity can be used to auto-calibrate the CD during long-term measurements. In addition, the design of the sensor allows for a redundant operation in contact CD. One of the multiple sensing electrodes can be used as a backup in case the primary electrode fails during a measurement session.

Designs for the electrical circuitry required to apply an ac voltage excitation signal, measure the resultant ac current signal, transduce, rectify, and amplify the signal are available in the literature and these will be used as a starting point for the GBWA data acquisition system. These designs will be modified for use in the GBWA. The primary modification is to develop low-power, battery-operated versions of the circuitry. A goal will be to reduce total power requirements to under 10 mA. This would provide 100 hours of operation from a pair of 9V alkaline batteries (500 mA/hrs each). Further run-time improvements will be incorporated in future versions. For example, by powering the electronics only during a measurement, a significant improvement in run-time is available. For example, it is likely that the measurement will only take 5 min, assuming an hourly measurement cycle, the run time is extended 12 fold (> 12 days). It should be noted that much of the electronic circuitry required for a field-deployable sensor would not be developed during this initial stage. For example, data storage and transmittal will be developed in consultation with an electrical engineer after this initial prototype is shown to work.

“Contact” Conductivity Detection. Two types of conductivity detection are available in the “contact” mode: “in-channel” and “end-channel”. In both cases, a number of detection electrodes are exposed to either the separation channel or the down-stream detection reservoir. In-channel detection uses electrodes in the separation channel while “end-channel” detection uses an electrode just outside the channel exit. In either method an ac signal of several kHz is applied *via* an oscillator across either a pair of detection electrodes or across a detection electrode and the low-voltage (i.e. ground) separation electrode. For safety the detection electrodes oscillator is decoupled from the high-voltage present in the capillary channel by use of capacitors or a transformers. The analytical signal is measured by the resulting current flow through either of the detection electrodes. Signal-to-noise ratio (SNR) is improved by use of band-pass filter prior to amplification. The detection electronics will be based on designs published by Zare’s group for use with in-channel²¹ and end-channel²⁰ detection. In principle, in-channel detection provides improved resolution and better SNR than end-column designs. However, the presence of the high electric field in the separation channel leads to practical difficulties. A typical separation field strength of 300 V/cm leads to as much as a 1.5 V dc potential drop across a 50 mm detection electrode. This can lead to electrolysis of the BGE due to the presence of anodic and cathodic local potentials on the detection electrode. Electrolysis can produce gas bubbles in the channel, which leads to poor separations. Solutions to this difficulty are proposed by use of thinner detection electrodes (minimizing potential drop) and by passivation of the detection electrode,

minimizing electrolysis. One proposed method of passivation is the electrodeposit a thin layer of polymer on the detection electrodes, for example, a phenolic polymer can be deposited by electrolysis of phenol in basic solution.²² Another proposed solution is use of lower separation fields. Lowering the separation field increases the separation time, but the benefit provided may be an acceptable trade-off.

“Contact-less” Conductivity Detection. Recent developments in conductivity detection suggest that an oscillometric or “contact-less” detection mode is suitable for use in CE detection.^{23,24} In contrast to in- or end-column detection, the electrodes are not directly immersed in the BGE, but are instead covered with a thin layer of dielectric material. The dielectric proposed for use here is silicon dioxide or spin-coated epoxy. Since the conductivity electrodes are not exposed to solution, they are immune from biofouling, electric field effects, and aging. As in in-column detection, a high frequency low-voltage ac voltage is applied across pairs of detection electrodes near the end of the separation channel. The voltage is coupled into the channel through the capacitance presented by the electrode and solution separated by the dielectric. Measurement of the voltage drop caused by the solution resistance between the detector electrode pairs provides the analytical signal. Since the capacitance between the electrode and solution is on the order of pF, high frequencies are required to decrease the capacitive reactance to levels comparable to the solution resistance. The solution resistance for a 0.1 M KCl BGE is about 30 kW for the channel geometry used here. (This assumes a 50 x 75 x 150 mm measurement channel with a specific conductivity of 1.3 S m⁻¹) It is likely that the resistance will be much higher for the CE experiments employed here. This suggests oscillation frequencies of up to 1 MHz may be necessary for good results. The high frequency required combined with a small analytical signal may make implementation difficult. A goal of this proposed work is to determine the feasibility of contact-less detection for the GBWA.

Related Research

A review of the USGS web site data base of state water resources research institutes projects revealed no active projects similar in scope or direction to this one. However, a significant number of projects are now in progress that are related to the prediction and management of NPS pollution movements in surface and ground water.²⁵⁻³² Most of these indicated the current lack of adequate temporal and spatial monitoring capabilities and the need for improved data resolution. As a fall back position, these investigators have approached the problem through predictions of nutrient movements based on minimal physicochemical data and computer models. All of these projects stress the importance of tracking nutrient and NPS pollution loads relative to temporal events in relation to water quality.

The analysis of nitrite, nitrate, and phosphate is typically performed by ion chromatography. Commercial companies such as Dionex sell instruments dedicated to ion measurement. These systems are large (~ 3 cubic feet), require large volumes of eluant and are incompatible with in-field operation.

Another technique that has seen significant development in the analysis of inorganic anions is capillary electrophoresis (CE). In this technique, separations are conducted in a buffer filled, fused silica capillary (50 to 100 mm in diameter and 50 to 75 cm in length) positioned between two buffer reservoirs. A high voltage power supply (0 to 30 kV) is connected between two reservoirs. Analytes introduced into the capillary, migrate at different rates under the influence of the electric field and are detected by one of several techniques (e.g. fluorescence, electrical conductance).

Several methods have been reported for the analysis of nitrites and nitrates using CE. Bories et al.³⁴, used CE to observed nitrite and nitrate levels in biological fluids. Complex matrix problems have been addressed by Fukushi et al.³⁵. In their study, nitrite and nitrate were separated and quantified in seawater. Most of the published techniques to date have used indirect detection schemes.³⁶ However, several electrochemical based detection schemes have been evaluated.³⁷

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