Portable, fully autonomous, ion chromatography system for on-site analyses

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ABSTRACT

The basic operating principles of a portable, fully autonomous, ion chromatography system are described. The system affords the user the ability to collect and analyze samples continuously for 27 days, or about 1930 injections before needing any user intervention. Within the 13 kg system, is a fully computer controlled autosampling, chromatography and data acquisition system. An eluent reflux device (ERD), which integrates eluent suppression and generation in a single multi-chambered device, is used to minimize eluent consumption. During operation, about 1 µL of water per minute is lost to waste while operating standard-bore chromatography at 0.5 mL min^{-1} due to eluent refluxing. Over the course of 27 days, about 100 mL of rinse water is consumed, effectively eliminating waste production. Data showing the reproducibility (below 1% relative standard deviation over 14 days) of the device is also presented. Chromatographic analyses of common anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}), is accomplished in under 15 min using a low backpressure guard column with ~25 mM KOH isocratic elution. For detection, a small capacitively-coupled contactless conductivity detector (C4D) is employed, able to report analytes in the sub to low micromolar range. Preconcentration of the injected samples gives a 50-fold decrease in detection limits, primarily utilized for in-situ detection of phosphate (LOQ 10 µg L^{-1}). Field analyses are shown for multiple on-site analyses of stream water indifferent weather conditions.

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1. Introduction

Developments in analytical instrumentation have seen the focus of measurement and analyses shift from the laboratory toward the field. The development of new, more versatile electronics and highly efficient components has been the driving force behind this trend [1,2]. Automated instruments in the field facilitate the ability to provide more reliable results with higher temporal resolution and reduced operating costs [3,4]. Most field instruments are designed to have sensitivities analogous to bench top instruments; yet, they are often smaller, more robust and easier to operate [3–5].

In environmental analyses, the demand for data collection over large areas and ranges of time, make autonomous instrumentation particularly favorable. The foremost problem with conventional analyses is the lag period between sample collection and analysis, which can often be problematic. Sampling on site and in real time is particularly beneficial in cases where product reliability or site conditions are the first priority [6]. In such cases, the advantages of autonomous field instruments become quite evident. This has given rise to a variety of automated, field portable devices.

One method, which has shown potential for ion analyses, is ion chromatography (IC). Several portable ICs have been reported demonstrating sensitivity levels necessary for environmental monitoring [7–10]. While many laboratory applications of IC have been described, relatively few field applications exist. Difficulties such as limited eluent capacity, high-energy requirements and cumbersome user involvement have significantly hindered the development of portable ICs. Since the first discussion of a portable IC [9], several approaches have been presented, which have discussed methods to increased IC portability [10–12].

When considering the portability of a field instrument, importance is placed on robustness as well as the extent of necessary user input. Of the previously described portable ICs, few discuss the inclusion of an autosampler [8]. Sample pretreatment prior to injection is both common and important in IC. In order to reduce weight, many of these systems have omitted autosampling equipment as well as data processing and storage electronics. Though eliminating these factors contributes to the compactness of the IC instrument, it also increases the need for user input. This can be undesirable in many monitoring regimes, especially those requiring continuous analyses.

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Developments in eluent reuse technologies, automation techniques and solar and battery technology have renewed the appeal of a portable IC system [2,13–15]. Together, these improvements have been successful in reducing user involvement and maintenance intervals while preserving device portability. Eluent reflux [16,17] has provided IC systems with a method to operate a standard-bore system while only producing water waste on a capillary system scale. Consequently, IC can be operated for extended periods while effectively eliminating the generation of chromatographic waste.

In addition to eluent reflux, automatic sampling and data collection has also reduced user involvement [2,18–20]. A computer controlled autosampler, injection system, and data recorder can support all functions, which previously required user assistance. This ability to sample continuously is especially important in environmental monitoring where variation between significant events can be unknown [3–6,21].

Increased instrument portability has also been aided by advancements in photovoltaic (PV) and battery technologies [22–26]. Together, these two principles have substantially reduced the need for access to grid power. These contributions in energy technology as well as eluent reuse have enabled the mobilization of a full IC system from the laboratory to the field. The physical, operational, and chromatographic properties of a completely autonomous field portable ion chromatography system are described in this paper.

2. Experimental

2.1. Physical instrument description

The total weight of the portable IC device used in this study weighed 27.5 kg including the battery and PV cell. The mounting surfaces were fabricated from aluminum sheets, which were mounted into a plastic case measuring $62 \times 48 \times 30$ cm (Southwest Public Safety, San Antonio, TX). All of the components were mounted into place using screws and aluminum mounting brackets. For the energy source, a 12 V 40 A h lithium ion battery (Smart Battery LLC., Tampa, FL) weighing 7 kg was used. The battery was combined with an 80 W polycrystalline solar panel (SolarTech Power Inc., Ontario, CA) weighing 7.5 kg. Together, the battery and PV cell provided enough energy to continuously power the system. When grid supplied power was available, a 40 W switch mode power supply (XP Power LLC., Sunnyvale, CA) was used to operate the device. This reduced the total weight of the device to 13 kg. A schematic of the chromatography system, including the autosampling system is shown in Fig. 1.

2.2. Eluent reuse

An eluent reflux device (ERD) was employed in the chromatographic system to recycle the eluent. This device described previously [16], uses multiple membrane separated resin chambers to integrate eluent suppression and generation into a single device. The ERD was capable of continuously generating and suppressing isocratic eluents, while generating virtually no chromatographic waste. By using recovered eluent in the analytical stream, a small volume of eluent could be reused multiple times over. With an ERD, the only source of eluent loss occurred during loop loading where the loop volume of KOH was lost to waste.

While the isolation of the electrodes provides the distinct advantage of a gas-free eluent, a separate reservoir must be used to provide an ion source to the electrodes. A small diaphragm pump, shown in Fig. 1, (KNF Neuberger AB, Stockholm, Sweden) was used to circulate de-ionized (DI) water from the electrode rinse reservoir through the electrode chambers at a rate of 0.5 mL min^{-1}.

Reservoirs containing 100 mL of ~25 mM KOH and 100 mL of DI water were used. The ERD was operated at a current of 28.5 mA in order to fully suppress the KOH eluent. At this current, water was added to the system via electrodialysis at a rate of 1.4 mL day^{-1}. To counteract the effect of eluent dilution from electrodialysis, a 3-port valve (DRV in Fig. 1) was placed at the conductivity cell outlet to remove water from electrodialytic addition. Assuming an injection volume of 23 μL and 4 injections per hour continuously, the instrument could operate for 27 days before reservoir refilling was necessary.

2.3. Flow arrangement and separation system

A mighty–mini pump (Scientific Systems Inc., State College, PA) was used to pump ~25 mM KOH eluent at a rate of 0.5 mL min^{-1}. In addition to the pump, a PEEK LO-Pulse, pulse damper (Scientific Systems Inc., State College, PA) was plumbed after the pump to remove pump pulsation. Eluent flow was directed from the pulse damper into an electrolytic eluent polisher described in [16], to remove ambient carbonate and other anions from the eluent stream (EEP as seen in Fig. 1). The EEP was used to strip anionic contaminants from the eluent, and continuously regenerated by the influx of hydroxide ions from the cathode. The polished (electrolytically purified), eluent then entered a 6-port, high-pressure injection valve (VICI Valco Instruments Co. Inc., Houston, TX).

From the valve outlet, flow was directed into a 4×50 mm AG15 column (Thermo-Fisher Dionex, Sunnyvale, CA). A guard column, rather than a standard analytical column was used to lower the back-pressure against the pump while still providing adequate analyte separations. The eluent then entered the ERD device [16], suppressing the eluent before the conductivity cell. After the suppressed eluent was measured, the flow was directed to a low pressure 3-port solenoid isolation or dilution relief valve (DRV in Fig. 1) (Bio-Chem Fluidics, Boonton, NJ), followed by an ATC-HC anion trap column (Thermo-Fisher Dionex, Sunnyvale, CA). To maintain eluent purity, an anion trap column was placed after the 3-port valve, which removed analyte ions post-detection. The analyte-free water then re-entered the ERD reflux chamber where the eluent was regenerated. The regenerated eluent then returned to the reservoir bottle for reuse.

2.4. Autosampling system

Samples were collected using a NE-500 syringe pump (New Era Pump Systems, Inc., Farmingdale, NY). A schematic of the autosampling process is shown in Fig. 2. Negative pressure was applied to the syringe passing the sample through a 0.45 μm filter (Whatman Polydisc GW, Sigma-Aldrich Co., St. Louis, MO). Once enough filtered sample was collected, a 3-port valve (Bio-Chem Fluidics, Boonton, NJ) directed sample to the injection valve. Before loop loading occured, the sample was first passed through a CTC-1, cation trap column (Thermo-Fisher Dionex, Sunnyvale, CA), and a HRP, organic trap column (Thermo-Fisher Dionex, Sunnyvale, CA) to remove any dissolved impurities. To reduce carryover, the injection valve remained in the normally closed position until the two trap columns were flushed with new sample. The injection valve then switched into the load position. A total of 1 mL of sample was loaded on an Ionswift MAC-200 monolith anion concentrator column (Thermo-Fisher Dionex, Sunnyvale, CA), with a 23 μL void volume. After loop loading, the 3-port valve switched back to normally open to collect the next sample.

2.5. Detection

The capacitively-coupled contactless conductivity detector (C4D) cell was constructed according to previous publications
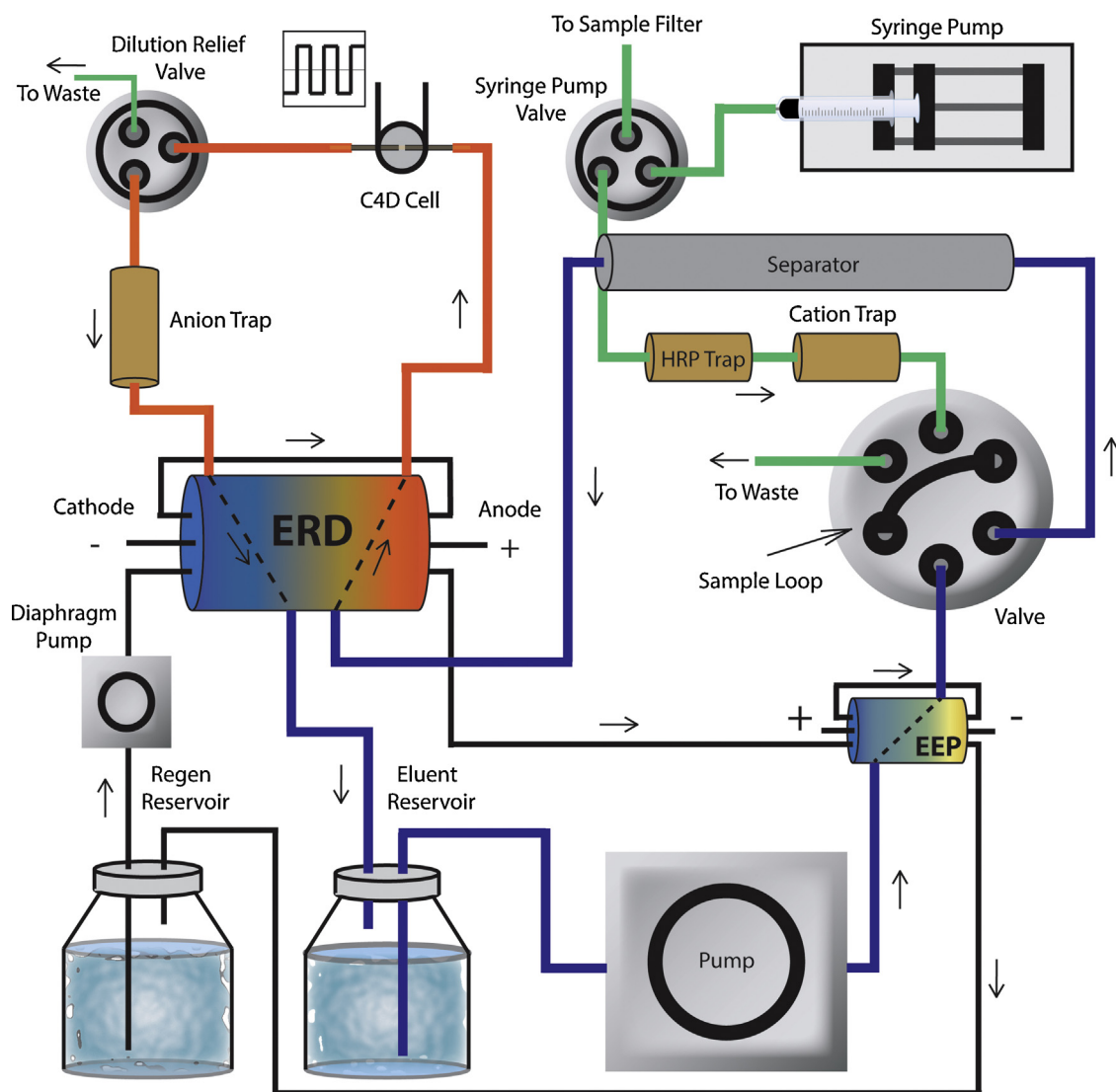
Fig. 1. *Instrument schematic.* Two separate reservoirs are deployed, one eluent and one regenerant water reservoir. The flow path of KOH eluent (blue), suppressed eluent (orange) and flow to and from the outside of the chromatography system (green), are represented by thicker lines. The electrode rinse water (black) is shown as the thin line. Arrows denote the direction of flow. Dashed lines in the eluent reflux device (ERD) and electrolytic eluent purifier (EEP) denote the approximate flow direction. Device polarities denote the net ionic movements in the electrodialytic devices. The 3-port dilution relief valve (DRV) removes excess water from the system to maintain a precise eluent concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
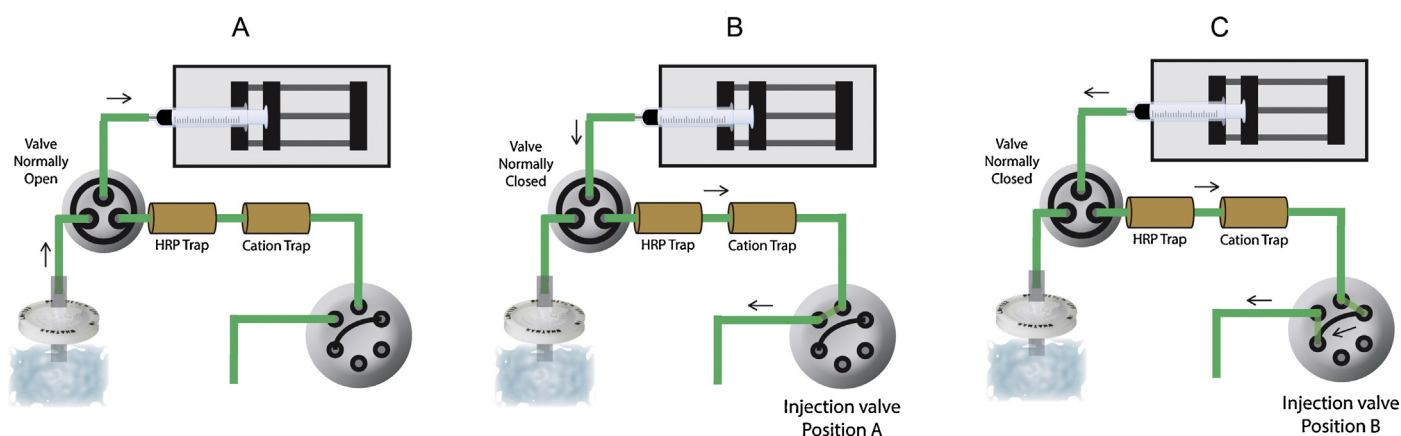
Fig. 2. *Autosampler schematic.* The autosampling process follows a three-step process depicted in this figure. In (A) the syringe valve in the normally open position allows flow into the syringe during sample collection. The syringe valve in (B) switches to normally closed position for sample pretreatment with the injection valve in the inject position. In (C), the injection valve switches to the load position to allow sample loading.
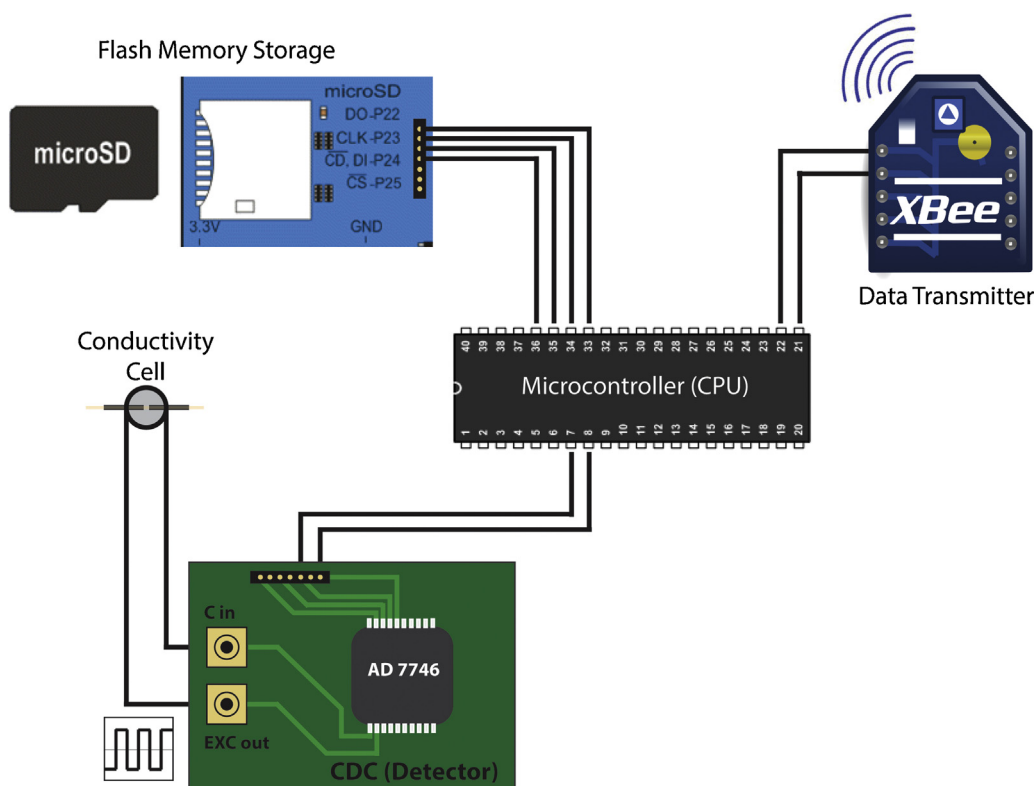
Fig. 3. *Data acquisition schematic.* The 24-bit values from the detector are sent to the CPU where they are converted into conductivity values. These values are passed from the CPU to flash memory where they are stored. The conductivity data is transmitted via XBee radio to a receiver located at the stationary PC for further processing. The CPU controls all processes simultaneously, included pumping and valve operations (not shown).

[2,12]. Ten centimeter of 536 μm ID/700 μm OD capillary (CM Scientific Ltd, Silsden, UK), was used along with two, 10 mm sections of 700 μm ID stainless steel 304 hypodermic tubing (Component Supply Company, Fort Meade, Fl) to construct the cell. Standard epoxy was used to hold the electrodes in place around the capillary at a distance of 0.75 mm. The entire C4D cell was placed in a Faraday cage to minimize any potential electrical interference. The cell was connected to an AD7746 capacitance to digital converter (Analog Devices, Inc., Norwood, MA), also described previously [2,12] by coaxial cable.

2.6. System control and data acquisition

The complete electrical system (designed and constructed in house) controlled all system components, including current regulation for the eluent polisher (EEP) and eluent reflux device (ERD). A Parallax propeller (Parallax Inc., Rocklin, CA) was used as the system CPU because of its ability to control multiple complex processes simultaneously. The propeller contains eight, 32 bit cores, which operate in parallel. A timing program was built into the CPU program to synchronize the various operations occurring in each core.

Data was acquired by calculating a conductivity value from the digital capacitance output of the AD7746. By using the glass capillary and electrodes described above, a small RC circuit can be formed [2,20]. In this model, the electrode-capillary interface represents the capacitor while the solution flowing inside the capillary represents the resistor. When a known signal is applied to the excitation electrode, the solution resistivity can be determined by the apparent capacitance of the capillary RC circuit [2]. Taking the reciprocal of the measured resistivity therefore gives the conductivity of the solution flowing through the capillary. The sampling of

the AD7746 operated at 32 kHz, which was averaged to provide a normalized 24-bit capacitance value when sampled by the microprocessor. The calculated conductivity data was collected at a rate of 5 Hz and stored numerically on an onboard 2 GB flash memory card. Four, 15 min chromatograms were produced each hour with each individual sample file contained about 20 kB of data prior to processing. In total over 90,000 samples could be collected before the onboard memory was full. In some cases, the system was also configured to transmit the date wirelessly via radio (Xbee PRO, Digi International Inc., Minnetonka, MN). Otherwise the Flash memory card could be manually removed and downloaded directly onto a Notebook computer (MacBook 6.1, Apple Corp, Cupertino, CA). The raw data was further processed using Origin 8.6 software (Origin Lab Corp., Northampton, MA). This software was used to integrate peak areas and calculate analyte concentrations from standard injections. A schematic of the data acquisition system can be seen in Fig. 3.

2.7. Reagents, resins and membranes

ACS grade potassium hydroxide pellets (Sigma-Aldrich Co., St. Louis, MO) were used to prepare the eluent and convert resins and membranes to their required forms. Laboratory distilled nitric acid was used for conversion to the hydronium form. The cation and anion resins used in the ERD were Dowex 50W × 4 and Dowex 1 × 4 200 mesh, respectively (Sigma-Aldrich Co., St. Louis, MO). The Excellionion exchange membranes were supplied by Snowpure LLC, San Clemente, CA. A more detailed description of the membrane and resin can be found in [16]. Anion standards were prepared in house using ACS grade reagents (Sigma-Aldrich Co., St. Louis, MO). The 4-anion standard solutions contained KCl, K_2SO_4, KNO_3, and KH_2PO_4. A high standard containing 5 μg mL^{-1}Cl$^-$,
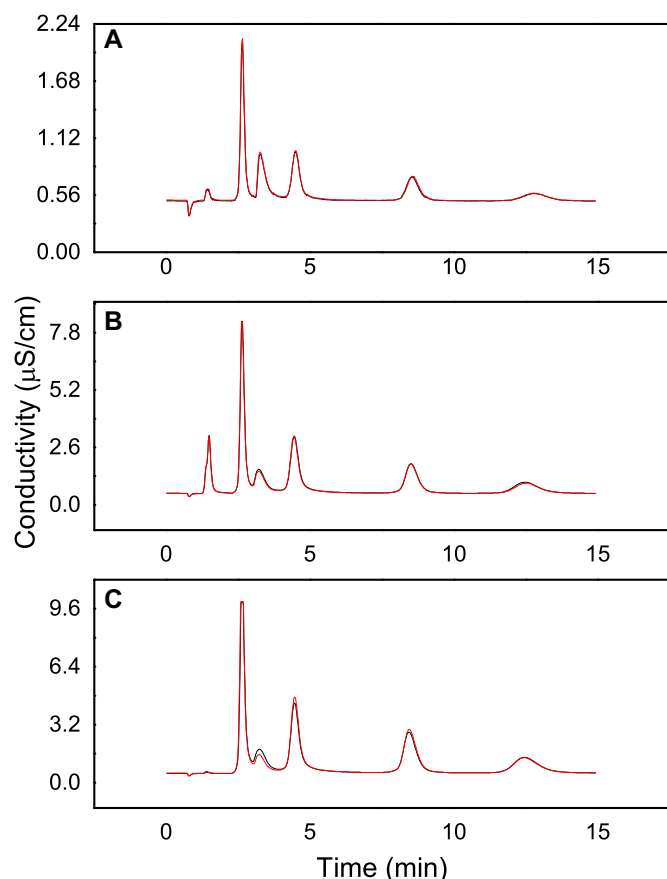
Fig. 4. *Chromatograms of 4-anion standards.* Three standard chromatograms were generated to calibrate and determine the linear range of the AD7746 detector. The 4-anion standard in (A) represents 0.5 μg mL^{-1} Cl$^-$, SO$_4^{2-}$, NO3$^-$, and 1.0 μg mL^{-1} PO$_4^{3-}$. (B) represents 2.5 μg mL^{-1} Cl$^-$, SO$_4^{2-}$, NO3$^-$, and 5.0 μg mL^{-1} PO$_4^{3-}$, and (C) represents 5.0 μg mL^{-1} Cl$^-$, SO$_4^{2-}$, NO3$^-$, and 10 μg mL^{-1} PO$_4^{3-}$. Two chromatograms for each standard are shown.

SO$_4^{2-}$ and NO$_3^-$, and 10 μg mL^{-1} PO$_4^{3-}$ was prepared. This standard was injected using a 20 μL injection loop. Less concentrated standards were also prepared by subsequent dilution of the original. Anion standard chromatograms are shown in Fig. 4.

3. Results and discussion

3.1. Power requirements

In any case where grid supplied power is not available, it is practical to have an instrument, which consumes minimal power. While the instrument described in this study is larger than previous IC instruments, it has the distinct advantages of being able to run autonomously and continuously for several weeks. The power requirements for the instrument are shown in Table 1. Like other IC systems, the eluent pumping system is overwhelmingly the most energy-consuming component. Unfortunately, the majority of the energy consumed by the eluent pump is lost as heat during the mechanical act of driving the pump piston.

During instrument operation the average power consumption was 22.5 W h. While the average power consumption was only 22.5 W h the maximum was 62 W h, which occurred during valve switching. Though this was only for ~30 ms intervals, the current draw more than doubled from 1.8 A to 5.2 A. It was found that while a large battery was not necessary when connected to grid power, a small 2 A h battery had to be placed in the system to supply excess current. In another configuration the instrument was configured to operate in a standby mode. During this period the power consumption was reduced appreciably to 5.8 W h. In certain monitoring regimes where high sample throughput is not necessary, this configuration can be quite useful. For example, if only a few samples are required during daily operation, the instrument could be configured to enter a standby mode between chromatographic operations. In addition to the reduced power consumption, reduced operation could utilize a smaller solar panel and battery.

3.2. Filtering, sample collection, sample preparation and preconcentration

Treatment of the samples before analysis was a critical step to ensuring the chromatographic reproducibility of the instrument. Without proper sample pretreatment ionic contaminants such as polyvalent cations and organic acids could irreversibly bind to the suppressor or chromatographic column, degrading their function. Highly charged organic acids, such as humics and fulvics, can bind permanently to the analytical column quickly reducing its capacity. In addition, analyte cations such as magnesium and calcium can displace monovalent potassium and hydronium, reducing suppressor capacity [16,17]. The autosampling system was designed to prepare the sample by removing these contaminants before

Table 1
Field IC system power requirements by component.

System component (12 V DC)	Power consumption (W h)		% Power consumption
	Active	Inactive	
Eluent pump	11.4	0.92	50.7
Electrodialytic eluent polisher	0.36–0.6	0	≤2.7
Injection valve (active 250 ms h^{-1})	0.03	0.9	<4.0
Eluent reflux device	0.36–0.6	0	≤2.7
Capacitance digital converter (AD7746)	0.06	0	0.27
Dilution relief valve (active 18.1 s h^{-1})	0.07	0.36	1.6
Electrode rinse pump	1.4	0.18	6.2
Syringe pump	2.8	0.6	12.4
Syringe pump valve (active 250 ms h^{-1})	0.001	0.36	1.6
System electronics	3.5	2.4	≤15.1
Radio data transmission	0.12–3.6*	0.001	0.5 (max 16*)
Operating power consumption	22.5 W h		
Standby power consumption	5.8 W h		
Battery capacity	480 W h		

All values were measured in watt-hours to calculate the average power consumption during a 15 min analysis period. The standby operating values represent the minimum power required to maintain instrument readiness. Power consumption for individual components are shown. The average power consumption for the instrument during operation is 22.5 W h while the standby power consumption is 5.8 W h.

injection. A 5 mL syringe was used to minimize the potential of significant carryover from previous samples. This was a necessary step because of the trap column and filter void volumes (500 and 700 μL, respectively). The syringe size was also important for applying the necessary pressure to properly load the sample onto the concentrator. Having a smaller cross-sectional plunger area significantly increases the syringe pumping pressure and loop loading time, which helps to conserve power.

Three milliliters of sample was drawn through a 0.45 μm filter to remove solid particles. After the sample passed through the trap columns, 1 mL of sample was loaded on the loop. Samples were preconcentrated to increase analyte sensitivity. Because the primary function of the field instrument was environmental monitoring, maximum sensitivity was essential. Generally, the measurement of phosphate at levels necessary for environmental monitoring was otherwise not possible without preconcentration. This can be seen in Fig. 4A where the phosphate concentration is 1.0 μg mL^{-1}.

3.3. Detection and data acquisition performance

The conductivity cell was optimized by adjusting the distance between the electrodes to 0.5 mm [2,12]. The response of the contactless cell was linear (R^2 = 0.991) with a baseline of 0.42 μS cm^{-1} and a 3 nS cm^{-1} peak–peak noise. Because of the limited range of the AD7746, the detector was only capable of a linear measurement from the detection limit ~15 nS cm^{-1} to 11 μS cm^{-1}. Based on the calibration data at the lowest level (Fig. 4A) and standard deviation of the baseline over a 15 min period, LODs were computed for the four analytes (S/N = 3). The limit of quantification (LOQ) for the four analytes were calculated in the same way using S/N = 10. These values are listed in Table 2. From these values it was determined that concentrating 1 mL of sample gave sufficient sensitivity for environmental analyses. Chromatograms of 3 different 4-anion standards are shown in Fig. 4.
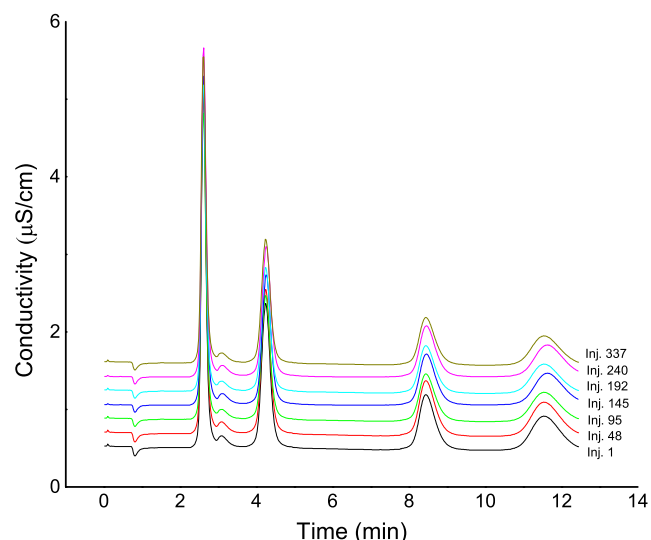
As with any instrument used in the field, changes in temperature must be considered. The AD7746 contained a built in thermometer, which was used for temperature compensation. The temperature data was collected along with each capacitance measurement and used to calculate a corrected conductivity. While the affects of temperature were not studied in detail, other studies have characterized the AD7746's ability to correct for baseline drift [12]. Using temperature compensation, conductivity measurements could be obtained regardless of the temperature from sample to sample.

The ability for the microcontroller to operate 8 processes simultaneously gave the propeller a distinct advantage in this application. While one core was operating the detector, another could calculate the conductivity from the capacitance measurement and write the value to flash memory. During the operation of the data acquisition system, two other cores were responsible for the rest of the system operation as well as the system clock. While the system was active only 5 of the 8 available cores were used.

Fig. 5. *Reproducibility over 14 days of continuous operation.* Selected chromatograms during 14 days of continuous operation (337 injections) measured in the laboratory. The chromatograms are offset 250 nS. Each chromatogram represents a 20 μL injection volume of 4-anion standard containing 5.0 μg mL^{-1} Cl$^-$, SO$_4^{2-}$, NO3$^-$, and 10 μg mL^{-1} PO$_4^{3-}$. The reproducibility for each peak was within 1% RSD, with PO$_4^{3-}$ being the worst (0.58% RSD). The eluent was ~25 mM KOH at 0.5 mL min^{-1} using an AG15 column.

3.4. Chromatographic reproducibility

In any IC system, the reproducibility is an important factor, which is determined by the instrument stability. This is particularly important in portable applications because of the autonomous nature of their operation. In the laboratory, standard chromatograms were generated for 4 anions over 2 weeks of continuous operation. This was done to limit any extreme variations in temperature, and to monitor several instrument stability parameters (i.e. eluent concentration, background conductivity and ERD current). System equilibration occurred 20 to 30 min after starting the instrument; the background conductivity stabilized at 0.42 μS cm^{-1}. The instrument was configured to inject one standard per hour for the entire time period. Fig. 5 shows the reproducibility of a selection of the 337 injections over 14 days. In Table 2, the retention times along with the relative standard deviation (RSD) of peak retention times over the 14-day period are shown. Injections were made using ~25 mM KOH eluent at a flow rate of 0.5 mL min^{-1}. While eluent reflux provides only isocratic capabilities, the long-term, continuous operation in a portable system provides a distinct advantage. Furthermore, isocratic elutions produced sufficient chromatographic separations at a practical rate. While a higher sample throughput could be attained using gradient analysis, there is not currently an established method, which is capable of recycling a gradient eluent.

Table 2
Analysis of chromatographic performance.

Analyte	Avg. Retention time (min)	Retention time RSD (%)	Peak width (min)	Limit of detection (mg L^{-1})	Limit of quantification (1 mL sample) (μg L^{-1})
Chloride	2.61	0.42	0.62	0.023	0.47
Sulfate	4.26	0.30	1.52	0.078	1.6
Nitrate	8.45	0.33	1.42	0.16	3.2
Phosphate	11.59	0.58	1.91	0.55	11

The average retention times and relative standard deviations of 7 selected 4-anion standard injections over 14 days of continuous operation. Detection limits were determined using a 20 μL injection volume of the lowest level calibration standard and the standard deviation of the baseline noise over a 15-min period. Quantification limits were determined using 1 mL of concentrated sample and the standard deviation of the baseline noise over a 15-min period. The signal to noise (S/N) ratio used in the LOD and LOQ determinations were 3 and 10, respectively.

Table 3
Comparison of the field IC versus laboratory IC performance.

Analyte	Field IC data (mg L^{-1})		Laboratory IC data (mg L^{-1})		Difference (%)	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Chloride	18.11	14.86	16.83	13.53	107.6	109.8
Sulfate	11.90	10.03	11.72	10.54	101.6	95.7
Nitrate	4.53	3.01	4.03	2.72	112.4	110.7
Phosphate	26.9*	64.4*	–	58.7*	–	109.7*

* Measured in µg L^{-1}.

Measured concentrations of 4 anions measured using field analysis and a standard laboratory ion chromatograph (IC). Sample 1 corresponds to the chromatogram in Fig. 6A while sample 2 corresponds to the chromatogram depicted in Fig. 6B. The % difference in values measured with the field IC versus values attained using the laboratory IC.

3.5. Field analyses

In an attempt to determine the chromatographic performance of the device in the field, several stream water samples were analyzed in-situ. The autosampler was programed to concentrate 1 mL of sample, as previously stated. Stream water samples from the same site were collected on two different days with distinctly different weather conditions. In Fig. 6A, an overlay of 3 chromatograms taken 2 h apart are shown during a period of low flow. The same sampling regime (3 chromatograms taken 2 h apart is shown in Fig. 6B. During the sampling in Fig. 6B, weather conditions were rainy, creating a period of higher flow. It is quite evident that the weather conditions had a significant effect on the total anion concentrations. Nitrate had an average peak height of 8.7 µS cm^{-1} in Fig. 6A while Fig. 6B show an average peak height of 2.1 µS cm^{-1}. Furthermore, within each chromatogram there are distinct differences in the concentrations of each anion indicating that the anion concentrations were changing within the sampling period. For example nitrate varied from 10.2 µS cm^{-1} to 7.3 µS cm^{-1} in Fig. 6A.

Water samples were also collected at the time of measurement for analysis in the laboratory. Table 3 shows the comparison of the laboratory and field portable IC units. While the measured values for the field portable IC are almost consistently higher, most of them are within 10% of the values reported in the laboratory, as seen in Table 3. Thus, it was determined that this instrument could be a suitable choice for field analysis.

4. Conclusion

This study has demonstrated the functionality of a completely autonomous and portable ion chromatography system capable of operating for weeks without user intervention. The system utilizes eluent reflux technology, which allows the same small eluent volume to be recycled without generating chromatographic waste. In fact, the system's autonomous operation is limited by the autosampler filtering system, not the eluent or waste capacity. Operating on 100 mL of eluent allowed the instrument to make over 6000 injections while the filter back-pressure limited the autosampler function after about 1900 injections. Regardless, the instrument was able to operate without user intervention for almost 4 weeks while collecting data continuously at 15-min intervals. The autonomous operation of the instrument was controlled by a multicore microprocessor, which integrated autosampling, chromatographic analysis, detection, and data acquisition procedures.

The main limitation of this system is the high-energy consumption of the eluent pump. Though advances in pumping technology are constantly developing, no significant advancements have been made on the scale necessary for standard bore chromatography. Not only could this limit the battery and solar panel sizes, but it could also reduce the instrument size substantially.

While this instrument is larger than its predecessors, the ability to operate continuously and autonomously compensates for its increased size. The system has proven to be a viable and practical device, especially in areas where high sample loads or large data sets are required. Regardless of this instrument's size, it is believed that such a system can uniquely offer continuous, on-site analyses without the production of chromatographic waste.

Though the IC system in this study was demonstrated for analysis of anions, cation analysis can easily be done with the changing of a few components. The astute reader can envision a system where the components in the eluent reflux device (ERD) are configured in such a way that an eluent capable of cation analyses is refluxed. Furthermore, the overall reproducibility, reliability, and efficiency were found to be analogous to laboratory bench top instruments. In closing, there is an ever-increasing interest for the further development of such systems for a range of applications.
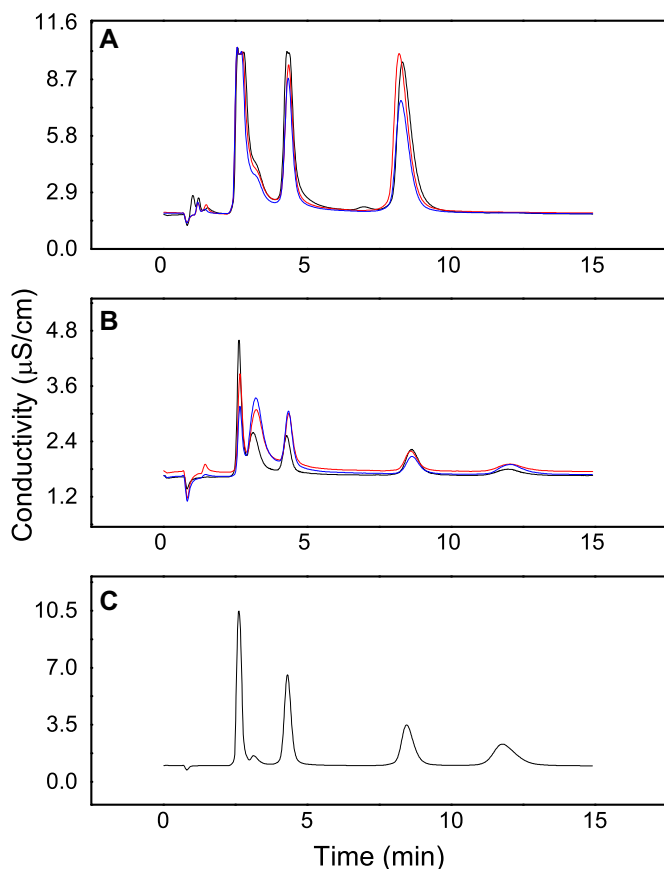
Fig. 6. *Chromatograms of field samples (stream water).* In-situ analyses under differential weather conditions. (A) depicts 3 chromatograms generated at 2-h intervals during a period of low flow, while (B) shows 3 chromatograms generated at 2-h intervals during a period of higher flow. A standard injection was also made at the field site for reference, shown in (C). Differences within ((A) and (B)) indicate dynamic conditions occurring in-stream.

Acknowledgments

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