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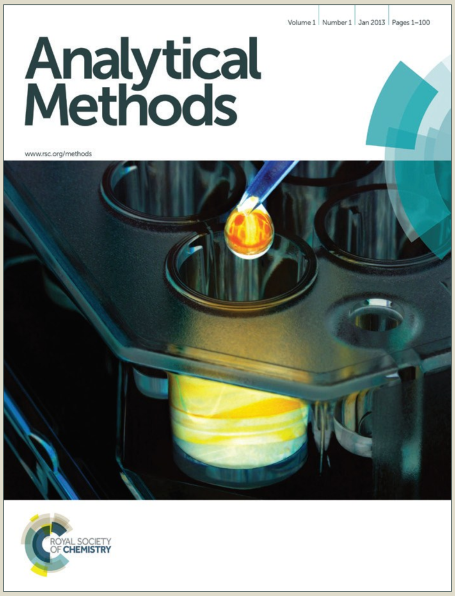

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Paper

Determination of Inorganic Anions in Oilfield Water Using Capillary Electrophoresis with Indirect Fluorescence Detection

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Analysis of high salinity oilfield water for anions presents challenges. Here we develop a capillary electrophoresis method using indirect fluorescence detection for simultaneous separation and determination of bromide, chloride, thiosulfate, nitrate and sulfate. 8-Hydroxypyrene-1,3,6-trisulfonic acid (HPTS) is used as the fluorescent probe in the background electrolyte. High resolution (8.5) between chloride and sulfate is achieved using an acidic BGE (pH 2.0) under reversed polarity. This method is capable of detection of trace anions in high chloride samples (5 ppm Br^- in 30 ppm Cl^-, 1 ppm NO_3^- in 400 ppm Cl^-, 1.5 ppm SO_4^{2-} in 1500 ppm Cl^-). Linear calibration (R^2>0.99) was achieved for sulfate in the range of 1~20 ppm in 500 ppm chloride. Limits of detection (LOD) were 0.4 ppm for sulfate and 1.4 ppm for chloride. This method was applied to the determination of chloride and sulfate in high salinity oilfield water samples, with 9% RSD for chloride and 84% spike recovery for sulfate.

1. Introduction

Oil production is the foundation for worldwide energy supplies. During oil production, oilfield water, also known as oilfield-produced water, is generated in large quantities[1] with 15 to 20 billion barrels of water produced per year in the United States of America alone.[2] Oilfield production water consists of formation water, flood water, and condensed water.[3] *Formation water* is naturally present in the reservoir. When the pressure within a well is not high enough for oil production, *flood water* is injected into the reservoir to pressurize and displace hydrocarbons. *Condensed water* is that collected upon removal of water vapor from produced gas.[4]

The chemical composition of oilfield water is very complex and varies from well to well. Oilfield water may contain various toxic compounds such as BTEX (benzene, toluene, ethylbenzene and xylenes), PAHs (polycyclic aromatic hydrocarbons), and organic acids.[4] Oilfield water may also contain very high concentrations of sodium chloride, and lower concentrations of anions such as sulfate and nitrate. The cost of producing, handling, and disposing of the oilfield water often defines the economic lifetime of a field and the actual hydrocarbon reserves.[2, 5] For example, pure water is not very corrosive to steel, while saline water increases the water conductivity and corrosion.[5] As a result, the wear of oilfield equipment and replacement costs increase with salinity.

Oilfield water is analyzed for a variety of purposes, including characterizing aquifers, evaluating environmental compliance, and monitoring corrosion and scaling.[2, 4, 5] Subsequent water treatment is guided by this analysis. Several classic methods of analysis are used to determine the anions in oilfield-produced water. Chloride, the major component of oilfield water salinity, is usually determined by Volhard titration.[5] However, any iodide or bromide present will be titrated as well. Sulfate, another major constituent of oilfield water, is measured gravimetrically after addition of barium. This gravimetric method is very time consuming.[5] Therefore, recent method development for oilfield water analysis has primarily focused on chromatographic methodologies. However such instrumentation is necessarily in the lab. Hence, there is increasing interest in the use of portable and field-deployable instrumentation for oilfield water sample analysis. Because the distance between sample collection and analysis can be minimized.

Ion chromatography (IC) is a very common tool for the determination of inorganic and small organic anions.[6-8] In chromatographic analysis, the high salinity of oilfield water sample presents a special challenge.[9-14] Analysis of sulfate and arsenate were affected by the high chloride matrix.[11, 15, 16] Cl^-, SO_4^{2-}, NO_3^-, I^- and Br^- determination in natural water matrix samples such as oilfield water, seawater and wastewater were achieved using a laboratory IC.[14, 17-19] For heavy duty, on-location analysis, a portable and autonomous instrument is preferred. However, limited eluent capacity and the weight of high-pressure pumps and components have limited the popularity of portable IC.[20, 21] Currently there is no portable IC that is suitable for on-location oilfield water analysis.

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Capillary electrophoresis (CE) is increasingly used for the analysis of a wide variety of analytes due to its speed and efficiency.[22-25] Compared to HPLC, CE has high resolving power, low cost operation, and simplicity in design, optimization and operation.[26] CE is also appropriate as a portable instrument as it has limited solvent consumption and lower weight. All of these advantages make CE a promising analytical technique for on-location oilfield water analysis.

CE has been widely used for inorganic ion analyses.[26-28] Recent developments in CE of inorganic ions have focused on high efficiency separations of anions and cations within complex sample matrices,[29, 30] use of alternative detectors,[27, 31] rapid and simple method development,[32, 33] and CE portability.[34-36] Several strategies have been employed for anion analysis in high salinity samples. UV absorbing anions (SCN$^-$, NO$_3^-$, I$^-$) were detected at ppm levels using a high chloride background electrolyte buffer (BGE).[37] However this method cannot detect non-UV absorbing anions such as sulfate and chloride, which are of primary interest in oilfield waters. Trace anions have also been pre-concentrated using transient isotachophoresis (tITP).[38-40] However, the leading electrolyte and terminating electrolyte needs to be deliberately chosen for each analyte ion.[39, 40] Hence, there is a need to develop a sensitive, universal anion analysis method suitable for portable CE of oilfield water samples.

To develop a universal method for all the inorganic anions, indirect detection was utilized in this work. Indirect detection is based on the displacement of a photometric (absorbing or fluorescent) ion present in the BGE by an analyte co-ion, resulting in a decrease in signal intensity.[41-43] Indirect UV absorbance detection has been widely used for inorganic anions.[44, 45] Recently, Donkor et al. developed a CE-indirect UV detection method for inorganic anion analysis in highly saline oilfield water.[46] In general, the sensitivity of indirect UV absorbance (10^{-5} to 10^{-6} M)[47-49] is poor. Indirect conductivity can achieve comparable or lower detection limits (10^{-5} to 10^{-7} M).[34, 50] However, conductivity detection requires isolation of the conductivity detector electronics from the high separation voltage, which complicates the system.[51] On the other hand, laser-induced fluorescence detection has been widely used in CE, with exquisitely low detection limits.[52, 53] To date, indirect fluorescence detection has seen very limited use in inorganic anion analysis. This is mainly due to the lack of appropriate fluorescent probes[45] and the stability of the light sources. Most fluorescent probes do not have mobilities that match those of inorganic anions, an important criterion in minimizing peak broadening.[54, 55]

In this paper, an indirect fluorescence detection method is developed and optimized for common inorganic anions in high salinity samples. 8-Hydroxypyrene-1,3,6-trisulfonic acid (HPTS) is used as the probe. A UV-LED is used as the light source. LEDs' small size, robustness, stable light intensity and low power consumption[56, 57] make them compatible with the needs of a portable capillary electrophoresis instrument.

2. Experimental

2.1 Chemicals

All solutions were prepared in Nanopure 18-MΩ water (Barnstead, Thermo Scientific, Marietta, OH, USA). 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), sodium sulfate, sodium bromide, sodium nitrate and sodium hydrosulfide hydrate were from Sigma-Aldrich (St. Louis, MO, USA). Sodium chloride (>99.0%) was from EMD Chemicals (Gibbstown, NJ, USA). Sodium thiosulfate was from Anachemia Canada (Montreal, QC, Canada). Sodium iodide was from BDH Chemicals (Toronto, ON, Canada). All the inorganic salts were prepared and stored as 10,000 ppm stock solutions. Formic acid was from Fisher Scientific (Fair Lawn, NJ, USA). All solutions were filtered (0.22 µm) before use.

2.2 Apparatus

Capillary electrophoresis was performed on a Beckman PA 800 plus Pharmaceutical Analysis system with an LIF detector (Beckman Instruments, Fullerton, CA, USA). Data acquisition (4 Hz) with normal filtering and control was performed using 32 Karat software for Windows XP on a Lenovo Thinkcentre computer. Fluorescence emission was collected using a 520-nm band-pass filter with a bandwidth of 20 nm (Beckman). The sample was injected hydrodynamically using 0.5 psi for 3 s. Untreated fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) with an inner diameter of 50 µm, outer diameter of 365 µm, and total length of 60.2 cm (50 cm to detector) were used. The capillary was thermostated at 25°C.

2.3 Light sources

The LED light source was a prototype Wilson Analytical High-Intensity Optically-Stabilized LED Light Source (Model: 405-2; Sherwood Park, AB, Canada). The LED emitter (LED Engin, San Jose, CA, USA) was set to 150.9 mW full output, and the central wavelength was nominally 405 nm. Collimation lens and a fiber coupler were used to efficiently transfer the light into the optical fiber. Round optical filters (12.5 mm) could be positioned between the LED and fiber coupler. An 450 nm O.D. 4 shortpass filter (Edmund Optics) was used to remove light above 450 nm from the spectral output of the LED.[58] A constant-current power supply was used to drive the LED. A visible-light measurement diode was placed facing the LED. This diode was connected to an optical feedback circuit that adjusts the LED light output power so that it is very constant, as will be shown in Section 3.1.

A violet diode laser from Laserglow Technologies (Toronto, ON, Canada) was also tested. The laser output was set at 20-39 mW, with a central wavelength of 406.4 nm with a wavelength tolerance of ±5 nm during warmup. The diode laser was warmed up for at least 30 min before use.

Both the LED and violet diode laser were connected to the Beckman instrument through a 2 meter-long, 3 mm O.D., 550/600 µm core/cladding fiber optic cable (OZ Optics Ltd. Ontario, Canada). A SMA 906 connector mates with the Beckman instrument and a SMA 905 connector mates with the light source.

To compare the power stability of the two light sources, baseline stability tests were carried out. The light sources were warmed up for 40 min before use. The capillary was filled with 0.4 M formic acid and the detector response was adjusted to zero. Then the solution (10 µM HPTS and 0.4 M formic acid) was hydrodynamically rinsed through capillary at 5 psi. The electropherogram was collected for 3 min at 520 nm at a data acquisition rate of 4 Hz with normal filtering. The peak-to-peak noise of the baseline was calculated after correction of baseline drift. Drift was taken as the slope of the linear regression of the baseline, and the noise was defined as the difference between the maximum deviation and minimum deviation in the baseline (Supplementary Figure S1).[59]

2.4 Procedures

New capillaries were pretreated with 1 M NaOH for 10 min (20 psi rinse), 0.1 M NaOH for 10 min (20 psi), and finally deionized water for 5 min (20 psi).

Chloride standard solutions of 50~800 ppm were prepared in BGE (0.4 M formic acid, 10 µM HPTS). For sulfate, standard solutions of 1~20 ppm were prepared in BGE containing 500 ppm chloride.

2.5 Oilfield water sample

Sample 11180 was a cloudy Bakken formation water sample, which contains 23,600 ppm chloride, and 75 ppm sulfate as determined by Wilson Analytical analysis. Oilfield water sample 11188 was a coffee-colored steam-assisted gravity drainage (SAGD) produced water sample with a pungent odor, containing greater than 100 ppm of chloride and 100 ppm sulfate as determined by Wilson Analytical analysis. The samples were preserved and transferred in Nalgene bottles at room temperature. In the Wilson Analytical analyses, chloride was determined by Volhard titration and sulfate was quantified by inductively coupled plasma-optical emission spectrometry (ICP) at 182.036 nm and 180.669 nm using a Varian (now Agilent, Santa Clara, CA, USA) ICP-OES instrument calibrated using 10 - 1000 ppm SO_4^{2-} standards. Prior to CE analysis, the samples were filtered (0.22 µm) and diluted with background electrolyte.

3. Results and discussion

Inorganic anion analysis using capillary electrophoresis (CE) with indirect photometric detection has been widely studied.[35, 43, 45, 49, 60] However, most of these applications have dealt with simple water matrices. The high salinity and variable nature of oilfield water presents a challenge for anion analysis. To facilitate the oilfield production and reduce the environment harm, a portable analytical instrument is demanded for heavy-duty field analysis for inorganic anions. CE is compatible with such requirements. Herein we develop a simple, easy-operation CE protocol for anion analysis that would be suitable for field analysis of oilfield water samples.

3.1 Laser stability study

For indirect fluorescence detection, the power stability of the light source is crucial.[42, 43] The theoretical concentration limit of detection (C_{LOD}) of CE-indirect detection is given by [42]

$$C_{LOD} = C_p/(TR \times DR) \qquad (1)$$

where C_p is the concentration of the relevant mobile-phase component, TR is the transfer ratio (the number of probe molecules displaced by one analyte molecule), and DR is the dynamic reserve (the ratio of the background fluorescence intensity to the noise).[42] The more stable the background signal (larger DR), the lower the C_{LOD} that can be achieved. Given that the fluorescence intensity is proportional to the excitation light intensity, any power fluctuation in the excitation light source will propagate into the baseline noise. Hence it is important to first develop a stabilized light source.

Both laser diode (LDs) and light-emitting diodes (LEDs) have been employed in portable CE instrumentation,[35, 36, 61-63] and are studied here. Laser diodes have been widely used for excitation in CE-LIF methods[64, 65] due to their great power stability, cost-efficiency and portability.[66] LEDs have also been used as light sources for fluorescence detection (LEDIF).[67, 68] The light emission in both cases is based on the same principle (p-n junction and carrier recombination in a solid state semiconductor). For blue light, LDs can in principle have high efficiencies at much higher input power densities than LEDs.[56] However, when used as an excitation light source for fluorescence detection, LEDs are much less expensive, more energy efficient and more stable (six times lower C_{LOD})[57, 67, 69] compared to diode lasers.[56, 67, 70, 71] To generate better stability with LEDs, an active stabilization was built into our LED light source, as mentioned in Section 2.3. To compare the power stability of the two light sources, 10 µM of the fluorescent probe HPTS was rinsed through the capillary and the baseline was monitored for both the diode laser and LED. Figure 1 shows a 180-s (720 data points) baseline segment void of any obvious perturbations. The diode laser yields a more intense signal (~0.63 RFU) compared to the LED (~0.44 RFU). However, the baseline noise, based on the drift-corrected peak-to-peak variation,[67] was 26 mRFU for the diode laser and 1.7 mRFU for the LED, consistent with the performance of LED in the literature.[67, 72-74] Hence, the DR of the LED (~250) is 10 times better than the diode laser (~25). Due to the superior stability performance of the LED, we used the LEDIF in all following experiments.

3.2 Detection of inorganic anions with HPTS

3.2.1 Selection of indirect fluorescent probe

The selection of indirect fluorescent probes for small inorganic anion involves two factors: the probe must be compatible with the excitation light source; and the mobility of the probe must be comparable to that of the analytes to minimize electrodispersion.[45, 75] This latter requirement ruled out many fluorescent compounds such as fluorescein due to their low mobility resulting from their large conjugated system and low charge. 8-Hydroxypyrene-1,3,6-trisulfonic acid (HPTS) was selected as the probe. The three sulfonate groups of HPTS (Figure 2) compensate for its large molecule size, making HPTS's mobility comparable with that of inorganic anions.[76, 77] HPTS has been used for the analysis of bromide, sulfate, nitrate and other inorganic anions.[76, 77] When the pH is lower than 5, the maximum excitation wavelength for HPTS is 403nm, matching well with the nominal emission bandwidth of the LED light source (405 nm). Previous optimization studies of 1-100 μM HPTS determined 10 μM HPTS to be optimal.[77] Preliminary studies herein corroborated these conclusions. Hence 10 μM HPTS was used in the rest of this work.

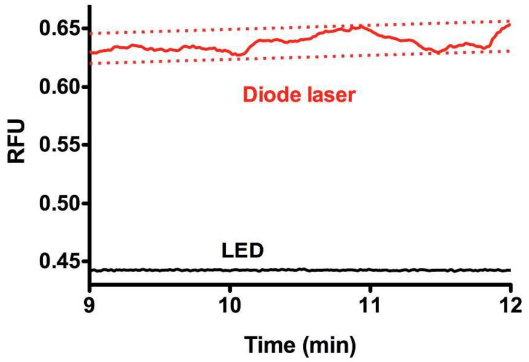

Figure 1 Comparison of baseline stability of diode laser and LED light source. Conditions: both light sources were turned on 40 minutes before use. Solution of 10 μM HPTS and 0.4 M formic acid, pH 2.0 was rinsed through capillary using 0.5 psi; capillary, L_T 60.2 cm, L_D 50 cm, I.D. 50 μm; detection, $\lambda_{excitation}$ = 405 nm and $\lambda_{emission}$ = 520 nm.

3.2.2 Selection of buffering agent

Resolution between chloride and sulfate in CE is challenging, as they have similar electrophoretic mobility.[78] In oilfield waters resolution will be all the more challenging given the large difference (10:1 - 2000:1)[79, 80] in the Cl^-/SO_4^{2-} concentration. Even addition of cationic BGE additives such as calcium[76] and phosphonium[32] generate low Cl^-/SO_4^{2-} resolution (<1 for calcium additive, no separation of Cl^-/SO_4^{2-} for phosphonium). Such low resolution is not suitable for heavy-duty, on-location field analysis of samples of varying matrix composition. One simple means of modifying inorganic anion mobility is pH. However of the common anions, pH has generally only been used to modify the mobility of nitrite (pK_a =3.15).[81-83] Recently de Macedo et al.[30] showed that at pH 2.0 the resolution between chloride and sulfate was enhanced. At this low pH, the sulfate is partially protonated ($pK_{a2} \approx 1.9$). Hence the mobility of sulfate is decreased. At the same time, the electroosmotic flow (EOF) is suppressed at pH 2.0, allowing the anions to counter-migrate against the EOF better and thus yield faster separations. Given the concentrated nature of oilfield waters, the BGE requires a buffer anion that is similar in mobility to Cl^- (7.92×10^{-4} cm^2/Vs) to minimize electromigration dispersion (Figure 2).

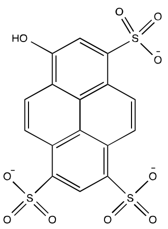

Figure 2 Structure of 8-Hydroxypyrene-1,3,6-trisulfonic acid (HPTS).

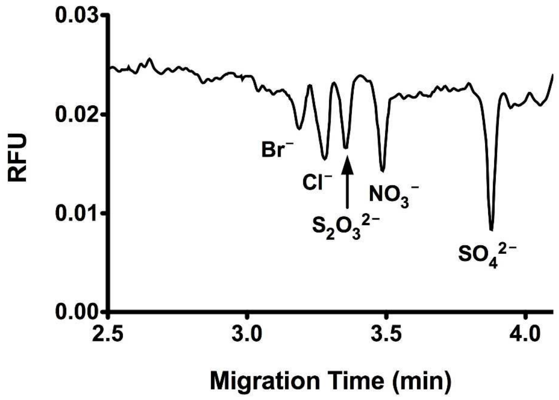

Figure 3 Separation of inorganic anions using HPTS at pH 2.0. Conditions: sample: 0.5 psi injection for 3 s of 10 ppm of Br^-, Cl^-, $S_2O_3^{2-}$,,NO_3^- and SO_4^{2-}; electrolyte, 10 μM HPTS and 0.4 M formic acid, pH 2.0; capillary, L_T 60.2 cm, L_D 50 cm. I.D. 50 μm; voltage, -22.5 kV; and detection, $\lambda_{excitation}$ = 405 nm and $\lambda_{emission}$ = 520 nm.

At the same time, high buffering capacity is needed. Formic acid (pK_a = 3.88, $\mu = 5.66 \times 10^{-4}$ cm^2/Vs) was previously used for low pH CE separations of chloride and sulfate.[30] As shown in Supplementary Figure S2 (A) increasing the concentration of formic acid increased the Cl^-/SO_4^{2-} resolution from 0.95 to 5.4, but decreased the sensitivity 30% (based on peak area) for both anions. The reduced sensitivity is due to the added formate ions competing with the target anions for the displacement of HPTS. As a result, the TR in Equation 1 for the target anions is reduced. 0.4 M Formic acid was chosen as the compromise between the resolution, buffering capacity, and sensitivity. The current was less than 30 μA and within the linear region of Ohm's plot in all experiments described below. Increasing capillary length (L_T) from 40.2 to 60.2 cm increased resolution between Br^- and Cl^- from 0.55 to 1.0 (Supplementary Figure S2 (B)). In summary, the conditions used for oilfield water analysis was a BGE of 0.4 M formic acid (pH 2.0) with 10 μM HPTS, and a capillary length of 60.2 cm (50 cm to detector), and an applied voltage of -22.5 kV.

3.3 Figures of merit

Figure 3 shows baseline separation was achieved at pH 2.0 for bromide, chloride, thiosulfate, nitrate and sulfate in less than 5 min. Iodide co-migrated with chloride and so cannot be resolved. Hydrosulfide and thiosulfate co-eluted at 3.34 min. Overall, the method is a relatively fast (~4 min) and simple (no additives or capillary coatings needed)[26, 33, 84-86] separation method for inorganic anions. Peak asymmetry was observed for the higher mobility anions (bromide, chloride) due to the mobility mismatch between these anions and the formate buffer.[76] The efficiencies (64,000 plates/m for bromide) are comparable with other indirect LIF-CE methods.[30, 76, 77] The resolution between chloride and sulfate in our method (8.5) is substantially better than indirect CE methods conducted at neutral to alkaline pH,[46, 76] and comparable to previous low pH indirect CE methods (resolution of 8.7).[30]

3.4 Anion Separations in High Salinity Samples

Electromigration dispersion of chloride in high salinity samples was significant resulting in a fronting peak (asymmetry factor B/A = 0.1 in Supplementary Figure S3) due to the difference in the conductivity between the sample zone and the surrounding background electrolyte.[87, 88] For other indirect CE methods developed for high saline samples,[27, 30, 46] the chloride peak asymmetry factor (B/A) was <0.2 for ≥200 ppm Cl^-, in agreement with Supplementary Figure S3.

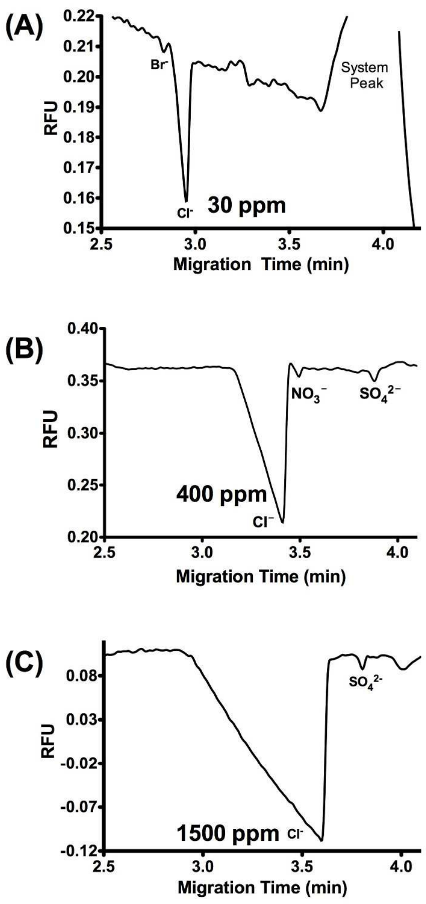

Figure 4 Anion analysis in high salinity samples. Samples (concentrations normalized to 5 s injection): (A) 5 ppm Br^- and 30 ppm Cl^-; (B) 1 ppm NO_3^- and SO_4^{2-} with 400 ppm Cl^-; and (C) 1.5 ppm SO_4^{2-} with 1500 ppm Cl^-. Conditions: injection, 0.5 psi; electrolyte, 10 µM HPTS and 0.4 M formic acid, pH 2.0; capillary, L_T 60.2 cm, L_D 50 cm. I.D. 50 µm; voltage, -22.5 kV; and detection, $\lambda_{excitation}$ = 405 nm and $\lambda_{emission}$ = 520 nm.

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This asymmetry ultimately limits the number of moles of chloride that can be injected without affecting sulfate detection (Supplementary Figure S3). As shown in Figure 4, electrodispersion was significant above 30 ppm Cl^-. Increasing the chloride concentration from 400 to 1500 ppm (for a normalized injection time of 5 s) increases the peak fronting, with the asymmetry factor dropping to 0.05 (Figure 4 (C)). This severe asymmetry makes detection of nitrate (a non-priority anion) impossible and determination of sulfate increasingly difficult. As the chloride concentration in oilfield waters range from 100 to 100,000 ppm,[79, 80] sample dilution is needed prior to CE analysis. To determine degree of dilution necessary for detection of trace anions in high salinity samples, the detection of bromide, nitrate and sulfate was tested with different chloride concentrations. Bromide was kept at 5 ppm, which is above the detection limit. The concentration of chloride was increased until the bromide peak could not be detected. Figure 4 (A) shows that bromide can be detected with concentration ratio of 1:6 to chloride. Similar experiments were performed for nitrate at 1 ppm and sulfate at 1.5 ppm. Figure 4 (B) shows nitrate can be detected with a ratio of 1:400 to chloride, and Figure 4 (C) shows sulfate can be detected better than 1:1000 of the chloride concentration. The sulfate result is comparable with another indirect UV CE method developed specifically for oilfield waters,[46] while our sulfate detection limit (0.4 ppm, see below) is lower due to the high sensitivity of fluorescence detection. The previous study did not investigate bromide or nitrate analysis in high salinity

Table 1 Calibration curve from chloride and sulfate standard solutions[a]

Analyte	Regression Equation[b]	R^2	Calibration Range	LOD
Cl^-	Y = (640±6) X – (6200±2500) [c]	0.9987	50~800 ppm	1.4 ppm
SO_4^{2-} [d]	Y = (690±7) X + (370±70) [d]	0.9989	1~20 ppm	0.4 ppm

a. Conditions: BGE, 10 µM HPTS and 0.4 M formic acid, pH 2.0; capillary: L_T 60.2 cm, L_D 50 cm, I.D. 50 µm; injection, 0.5 psi for 5 s; voltage, -22.5 kV; detection, $\lambda_{excitation}$ = 405 nm and $\lambda_{emission}$ = 520 nm.

b. Regression equation: the dependent variable (Y) is peak area while the explanatory variable (X) is the analyte concentration in ppm.

c. Chloride calibration: The intercept is statistically equivalent to 0 within the 98% confidence interval.

d. Sulfate calibration: 500 ppm chloride was present in all standard solution to mimic the matrix effect. The intercept does not lie within the 99% confidence interval.

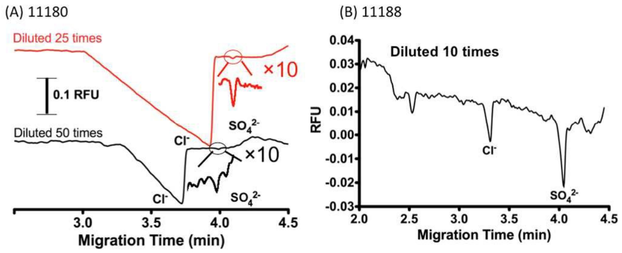

Figure 5 Electropherograms of a Bakken formation sample (A) and an enhanced oil recovery sample (B). Samples were filtered and diluted with BGE as per Section 2.5. Dilution factors are indicated in the figures. Conditions: injection, 0.5 psi for 5 s; BGE,10 µM HPTS and 0.4 M formic acid, pH 2.0; capillary, L_T 60.2 cm, L_D 50 cm. I.D. 50 µm; voltage, -22.5 kV; and detection, $\lambda_{excitation}$ = 405 nm and $\lambda_{emission}$ = 520 nm.

samples.[89]

To evaluate the effect of a high chloride matrix on sulfate quantification, calibration of sulfate was carried out as per Section 2.4. For standards containing 500 ppm chloride, the calibration curve for peak area of sulfate was linearly related to concentration over the 1-20 ppm range studied (Table 1), with a limit of detection of 0.4 ppm. The residual plot indicated linearity of response. This range is comparable with other indirect LIF detection methods for samples without high salinity.[43, 60, 76, 77] With those methods, sulfate could only be detected for <200-fold Cl^-/SO_4^{2-} ratio due to the limited resolution (Rs<4) between these anions.[87, 90]

3.5 Analysis of oilfield waters

Two oilfield water samples were analyzed using the developed method. Peaks were identified by comparison of the migration times with those of standards. Quantification was done using peak areas compared to external calibration containing 50-800 ppm Cl^- and 1-20 ppm SO_4^{2-}. Figure 5 shows the analysis of a Bakken formation (A) and a stream assisted gravity drainage (SAGD) enhanced oil recovery (B) sample. For Bakken formation water at 50 times dilution, the sulfate peak was difficult to distinguish from the baseline. Hence the chloride and sulfate concentration were quantified with a dilution factor of 25. Table 2 shows the CE method yielded comparable chloride concentrations to the Volhard titration. Further dilution of the sample (total of 250 fold) enabled resolution of bromide and nitrate peaks from the chloride matrix. However no bromide or nitrate was detected (< 250 ppm in original sample). For the SADG sample (Figure 5 (B) and Table 2), there is excellent agreement in the chloride concentration with a RSD of 9%.

A systematic bias is evident in Table 2 in the analysis of sulfate by CE versus the ICP analysis, with the CE results being much lower. ICP measures the total sulfur in the sample. Thus other sulfur-containing species within the sample would also be reported as sulfate.[5, 14] The negative bias in sulfate determination is also observed in a recent indirect CE-UV method designed for oilfield water analysis.[46]

Table 2 conventional methods versus CE quantification result of samples

Sample	Conventional (ppm)		CE Mean ± S.D. (ppm) n=3	
	Chloride (titration)	Sulfate (ICP)	Chloride	Sulfate
Bakken[a]	23600	75	28600 ± 400	15 ± 5
SAGD[b]	160	300	174 ± 15	127 ± 3

a. Bakken formation water sample was diluted 25 times before quantification.

b. SADG sample was diluted 10 times before quantification.

Spiking the Bakken formation sample with 10 ppm SO_4^{2-} yielded a recovery of 84%. Hence, we are confident that our sulfate quantification values are more accurate than the ICP results.

4. Conclusions

We developed and optimized an easy operating, simple-procedure anion analysis method using indirect fluorescent detection-capillary zone electrophoresis suitable for on-location oilfield water analysis. 8-Hydroxypyrene-1,3,6-trisulfonic acid (HPTS) was used as the fluorescence probe. The high stability of a 405 nm light emitting diode (LED) yielded a stable fluorescence background suitable for indirect detection. Baseline separation of bromide, chloride, thiosulfate, nitrate and sulfate under low ppm concentrations was achieved. Identification of bromide, nitrate and sulfate in high saline (≥30 ppm Cl-) samples was accomplished. Analysis of oilfield water samples was achieved.

Acknowledgements

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Analysis of high salinity oilfield water for anions presents challenges. Here we develop a capillary electrophoresis method using indirect fluorescence detection for simultaneous separation and determination of bromide, chloride, thiosulfate, nitrate and sulfate. 8-Hydroxypyrene-1,3,6-trisulfonic acid (HPTS) is used as the fluorescent probe in the background electrolyte. High resolution (8.5) between chloride and sulfate is achieved using an acidic BGE (pH 2.0) under reversed polarity. This method is capable of detection of trace anions in high chloride samples (5 ppm Br^- in 30 ppm Cl^-, 1 ppm NO_3^- in 400 ppm Cl^-, 1.5 ppm SO_4^{2-} in 1500 ppm Cl^-). Linear calibration (R^2>0.99) was achieved for sulfate in the range of 1~20 ppm in 500 ppm chloride. Limits of detection (LOD) were 0.4 ppm for sulfate and 1.4 ppm for chloride. This method was applied to the determination of chloride and sulfate in high salinity oilfield water samples, with 9% RSD for chloride and 84% spike recovery for sulfate.

An example of portable LED fluorescence spectrometer unit from Wilson Analytical