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Determination of boron concentration in oilfield water with a microfluidic ion exchange resin instrument

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ABSTRACT

We developed and validated a microfluidic instrument for interference-free determination of boron in produced water. The instrument uses a boron-specific chelating resin to separate the analyte from its complex matrix. Ten produced water samples were analyzed with the instrument and the results were successfully validated against ICP-MS measurements. Removing interference effects enables precise boron measurement for wastewater even with high total dissolved solid (TDS) levels. 1,4-Piperazinediethanesulfonic acid conditions the resin and maintains the optimum pH for boron adsorption from the sample. Boron is then eluted from the resin using a 10% sulfuric acid solution and its concentration measured with the colorimetric carminic acid assay in 95% sulfuric acid. The use of a microfluidic mixer greatly enhances the sensitivity and kinetics of the carminic acid assay, by factors of 2 and 7.5, respectively, when compared against the same assay performed manually. A maximum sensitivity of $2.5 \text{ mg}^{-1} \text{ L}$, a precision of 4.2% over the $0–40.0 \text{ mg L}^{-1}$ measuring range, a 0.3 mg L^{-1} limit of detection, and a sampling rate of up to four samples per hour were achieved. Automation and microfluidics reduce the operator workload and fluid manipulation errors, translating into safer and higher-quality measurements in the field.

1. Introduction

Forty-seven percent of the hydraulically fractured wells in the United States are located within a water-stressed area [1]. Hydrocarbon production alone produces 210 million of barrels of water per day [2]. Reclaiming this huge volume of oilfield wastewater to reduce freshwater dependency in water-scarce areas is an environmental and economic challenge. Recent trends indicate that produced water can be treated and reused for irrigation and industrial applications instead of being disposed of in a reinjection well [3]; however, sufficient characterization must take place. The fate of produced water is strictly regulated [4, 5] and the presence and level of potential pollutants must be determined before repurposing the water. Oilfield water composition is complex and is usually characterized by the presence of organic matter and high total dissolved solid (TDS) levels. TDS levels of up to 40% can be encountered [6]. Of specific interest is boron. Boron can be encountered in produced water in concentrations higher than 400 mg L^{-1}. It is a micronutrient necessary at low concentrations but can have harmful effects on flora at high levels. Crops and

plants present different tolerance levels ranging from below 1 mg L^{-1} (almonds, apple trees) to greater than 1000 mg L^{-1} (*Puccinellia distans* and *Puccinellia frigida*) [7–9]. Boron concentration is a critical measurement because the concentration impacts the repurposing of produced water. Precise onsite measurement is crucial to enable a rapid and informed business decision.

For a detailed review of the existing measurement methods and instruments for boron in water, the reader is referred to the work of Sah and Brown [10].

For water and wastewater analysis, the recommended methods listed by the United States Environmental Protection Agency (EPA) [11] are inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). EPA recommends the sample to have no more than 0.2% TDS for optimum measurement. Thus, dilutions by a factor 1000 or 10,000 are common practice. ICP-MS and ICP-OES fare very well in laboratory environments but have limited applications in remote field locations due to their physical footprint and cost of operation.

Manual colorimetric assays are the current measurement approach utilized in remote oilfield locations. Colorimetric assays for boron are reviewed in Floquet et al. [12]. The operator is trained in using readily available glassware and simple chemistry equipment to perform measurements as the need arises. Precision, accuracy,

repeatability, and measurement frequency depend on the operator skills and expertise and the operator's ability to distinguish subtle color differences or titration end-points. Automation of the assays would minimize operator dependency, allow for a better control of the chemical reaction, and improve sample turnover and measurement quality.

A major drawback of colorimetric assays is their susceptibility to chemical interferences. This is an often overlooked and serious issue due to the complex and rapidly changing composition of produced water. Various mitigation plans to reduce the effect of chemical interferences were reported in the literature. For example, solvent extraction is a popular but laborious technique [13–17]. Also, the addition of masking agents is commonly reported. Amongst the mitigation methods, the use of ion exchange resins to isolate the boron from its matrix is a widespread technique, with reports starting as early as 1954 [18, 19]. Two approaches are commonly encountered. An ion exchange resin adsorbs the unwanted ions and lets the simplified matrix with its boron content pass through for further determination [18, 20, 21], or a boron-specific resin adsorbs the boron from the matrix, requiring an elution stage to quantify the analyte concentration [22–24]. Because the composition of produced water changes rapidly over a wide span of potential interferents, we favored the latter approach.

Several instruments were reported using combinations of conversion to tetrafluoroborate with detection by an ion selective electrode [17] or by ion chromatography (IC) [25, 26]. Also, multiple ion exchange resin-based instruments followed by determination of boron by atomic absorption spectrometry [20] or conductivity measurements [21], and IC with a sorbitol eluent [27] were reported. All of these instruments were used in applications where the interfering matrix was well characterized and changed very little. Of particular interest is the work of Skerka and Lechner [24], who used a boron-specific ion exchange resin coupled to azomethine-H as a reagent to produce a fully automated instrument capable of measuring boron in low concentrations ($< 0.2\ mg\ L^{-1}$) in natural waters. They used ethylenediaminetetraacetic (EDTA) as an agent to mask metal ions. The reagent needed to be prepared on a daily basis and stored in a refrigerator and away from light sources even while being used, making it difficult to use in remote locations where ruggedized methods and apparatus are required. Preparing the reagent automatically and on demand is possible, as described by van Staden [28], but adds additional complexity and reliability risks.

In our previous work, we optimized and demonstrated the use of the carminic acid assay for the manual determination of boron in oilfield waters [12]. The carminic acid assay is a single-step assay [29–32] with a shelf life greater than two months and very little sensitivity to environmental conditions. The reagent turns from red to purple in the presence of boron. The color change is proportional to the boron concentration and follows the Beer-Lambert law. The peak sensitivity is recorded between 610 and 660 nm. Interferences from dissolved strontium, calcium, titanium, and zirconium is minimized but still exist, and high chloride concentrations lead to sample evaporation when mixed with the reagent.

In this work, we address the operator-related performance issues by automating the measurement protocol and overcome the chemical interferences by integrating a boron-specific chelating resin in the system. We present and validate a microfluidic-based instrument capable of measuring boron concentration in produced water, in the field, in an interference-free manner. We also demonstrate how the use of microfluidic technology improved the sensitivities and reaction times of the carminic acid assay. The instrument is intended to be used for ad-hoc measurements on produced water stored in tanks, where a batch analysis can be performed.

2. Experimental section

2.1. Chemicals

All the chemicals were purchased from Sigma Aldrich Canada and stored in polypropylene containers. To obtain a $1\ g\ L^{-1}$ reagent, 250 mg of carminic acid (CAS 1260-17-9) were dissolved into 250 mL of 99.999% sulfuric acid (CAS 7664-93-9). 1 L of eluent (10% sulfuric acid) was prepared by diluting 100 mL of 99.999% sulfuric acid into 900 mL of deionized water. To prepare the pH buffer, 173 g of 1,4-piperazinediethanesulfonic acid (PIPES, CAS 5625-37-6) were dissolved into 1 L of deionized water. The pH of the PIPES buffer was adjusted to 6.8 by adding pellets of sodium hydroxide (CAS 1310-73-2). The $1000\ mg\ L^{-1}$ boron standard stock solution was prepared by dissolving 5.6364 g of boric acid (CAS 10043-35-3) into a 1 L class-A flask filled with deionized water. Lower concentration standards were prepared by diluting the stock solution into the required PIPES buffer volume. All the water samples were diluted by a factor 10 in PIPES buffer to standardize the method.

For the interference study, chloride salts of calcium (CaCl$_2$, 2H$_2$O, CAS 10,035-04-8), magnesium (MgCl$_2$, 6H$_2$O, CAS 7791-18-6), potassium (KCl, CAS 7447-40-7), sodium (NaCl, CAS 7647-14-5), and strontium (SrCl$_2$, 6H$_2$O, CAS 10,025-70-4) were dissolved in deionized water to make up the stock solutions. $1000\ mg\ L^{-1}$ standards of zirconium, titanium, and iron were purchased from Delta Scientific, Canada and diluted as required.

2.2. ICP-MS

ICP-MS measurements were provided by Alberta Innovates–Technology Futures (AITF) in Vegreville, Canada. A PerkinElmer Elan DRC-II ICP-MS equipped with a high-throughput Elemental Scientific (ESI, Omaha, USA) SC-FAST flow injection 8DX auto-sampling system was used. Upon receiving the samples, for ICP-MS measurement, AITF added nitric acid as a standard protocol for sample preservation. The addition of nitric acid to the sample was specific to AITF's protocol for ICP-MS measurement and followed EPA recommendations [11]. Sample acidification was not needed for the microfluidic ion exchange resin instrument and method described in this manuscript as it would precipitate when in contact with PIPES buffer. Therefore, for ICP-MS measurements, the samples were prepared in deionized water. The sample preparation by AITF was performed in a class-100 laminar fumehood and filtered using a 0.45 μm membrane filter [11]. The samples were diluted by factors of 1000 to 10,000 to overcome the measurement errors associated with samples having TDS values higher than 0.2% (w:v) and peak overlap due to chemical species present in high concentrations [33].

2.3. Manual carminic acid assay

The manual carminic acid (CA) colorimetric assay was performed as described in Floquet et al. [12]. The CA was mixed at a 5:1 reagent-to-sample mixing ratio in a 10 mm quartz cuvette (Starna Cells Inc., Atascadero, USA, 21−Q-10, 10 mm Spectrosil quartz with PTFE stopper). After shaking, the solution was left to rest and develop for 30 min at ambient temperature. A calibration curve was prepared prior to measuring the samples. The spectrophotometric system was composed of a UV–vis deuterium tungsten halogen light source (DT-MINI-2GS, Ocean Optics, Dunedin, USA) attached to a cuvette holder via a fiber optic and a USB spectrometer (HR4000+, Ocean Optics) to measure the light intensity. Absorption was computed using 660 nm as a measuring wavelength and 865 nm as a reference wavelength to account for baseline drift.