Determination of transition metal ions in fossil fuel associated wastewaters using chelation ion chromatography

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Abstract and Keywords

This study outlines the development and subsequent validation of a method using chelation ion chromatography (CIC) pretreatment followed by traditional ion chromatography (IC) and post column UV/vis detection to measure transition metals in fossil fuel wastewaters, such as oil & gas (O&G) brines and coal mine drainage (CMD) waters. Measurement of transition metals is often an important characterization step in the research of environmental and energy systems. IC represents one way to measure these metals with the advantages of being versatile, simple and relatively low cost compared to other analytical methods. However, high concentrations of alkali and alkaline earth metals present in fossil fuel wastewaters will decrease IC detectability of transition metals in these waters. In this study, a CIC method was developed for the analysis of transition metal ions (Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, and Fe^{2+}) in fossil fuel associated wastewaters such as Appalachian CMD and O&G wastewaters from the Permian and Bakken shale basins in the United States. CIC system incorporated an on-line chelator column (e.g., the MetPac CC-1) with high selectivity for transition metals over alkali and alkaline earth metals for salt matrix removal prior to transition metal separation and detection. Additional method developments also included acidifying all samples to 2% v/v HCl and using gradient elution rather than isocratic. The recoverability of transition metals in simple salt solutions commonly found in CMD and brine samples (e.g. NaCl, Na_2SO_4, $CaCl_2$) using CIC was evaluated and compared to that using traditional IC. Our results found that the CIC system significantly improved transition metal recoveries for samples in 10,000 mg/L $CaCl_2$ matrix, reaching 87%-108% recovery for all analytes, as opposed to 2-323% recovery in traditional IC. The limits of detection in this study achieved 10.09 – 161.2 μg/L, comparable to reported values in similar IC studies. The developed method was also verified with certified water samples, resulting in 89% - 111% recoveries in samples with higher analyte concentrations (i.e. >4x the LoDs). The developed method achieved 87% -112% recoveries for most analytes in CMD samples and 72%-138% recoveries for Bakken shale samples, relative to ICP-MS values. Overall, the current IC method can be a very good screening tool for fast and cheap analysis for transition metals at mg/L level, to facilitate selection of samples for more detailed ICP-MS analysis.

Keywords: Chelation ion chromatography; coal mine drainage; oil and gas brine; transition metals

1. Introduction

In environmental and energy systems, identifying and quantifying the ionic composition of collected aqueous samples is an important characterization step that is essential for further research. Among the ions found in environmental and energy systems are the transition metals Co^{2+}, Cu^{2+}, Fe^{3+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}. Many of these have been shown to serve not only as nutrients for organisms at healthy levels [1,2], but also as environmental pollutants at excessive levels [3]. The presence of transition metals in the environment is primarily the result of natural mineral weathering. In addition, industrial activities such as mining and fossil fuel extraction can contribute to abnormally high levels of transition metals in impacted water systems [1,2,4]. Wastewaters from these fossil fuel extraction activities, such as coal mine drainage (CMD) and oil and gas (O&G) wastewaters, often contain transition metals at concentrations of multiple orders of magnitude higher than natural waters (e.g. seawater), presenting significant environmental problems [5–7]. Furthermore, O&G wastewaters can contain even higher concentrations of Na, Mg, K, Ca and Al than seawater, which can introduce complex sample matrices for transition metal detection in multiple analytical techniques [5].

Popular instrumental techniques to measure transition metals include atomic absorption spectroscopy (AAS), graphite furnace AAS (GFAAS), inductively coupled plasma – atomic emission spectroscopy (ICP-AES) and mass spectrometry (ICP-MS), colorimetric, and electrochemical methods [8–10]. The approach presented in this study for transition metal quantification is high performance ion chromatography (IC) combined with colorimetric detection. This technique affords the benefits of being versatile and common in most labs, being relatively low cost, and having the potential to differentiate among different redox species of the same element (e.g., Fe^{3+} and Fe^{2+}) [8,11–13]. Ion chromatograph (IC) systems are often used to measure major anions and cations in analytical labs. To expand its capability for transition metal detection, a UV-vis spectrometry unit can be attached at the end of the flow line on IC. The cost of adding parts to an existing system can be significantly less compared to purchasing a separate instrument for transition metal detection.

Research has shown that the presence of alkali and alkaline earth metals, especially Ca and Mg, can impact detection of transition metal ions. For instance, Ding et al. (2000) stated that concentrations of Ca, Mg greater than 10 mg/L resulted in increased retention times of transition metals. Murgia et al. (2011) found that concentrations of Ca, Mg greater than 250 mg/L results in amalgamation of Co, Cd, and Mn peaks making them unquantifiable [10,14,15]. These concentrations of alkaline earth metals are common in fossil fuel wastewaters. Therefore, additional pretreatment is needed to deal with potential interferences induced by alkali and alkaline earth metals.

A proven solution to dealing with high ionic strength matrices is pre-treatment with chelation ion chromatography (CIC) [13][13,16] Chelation columns can be incorporated into an HPIC system to carry out the pretreatment automatically online, a technique pioneered by Siriraks and Kingston [17]. They used the MetPac CC-1 (ThermoFisher Dionex, Inc.), which is still available today. This column contains iminodiacetate functional groups, which preferentially chelate lanthanides, heavy, and transition metals over alkali and alkaline earth metals during the sample injection [18]. These targeted metal analytes are then later removed from chelator column onto the separator column using an acid eluent [17,19,20]] or an eluent containing a stronger ligand [21]. This technique has since been employed for the analysis of transition metals in a variety of different samples, such as seawater, freshwater, wastewater, plant and animal material, soils, etc. but to our knowledge has not been applied to O&G wastewater or CMD [4,19,21–23].

One prior study did use a different CIC technique for the analysis of alkali and alkaline earth metals in oil-well brines, but did not attempt to measure transition metals [24].

This paper outlines the development and subsequent validation of a method using CIC and IC followed by post column UV/vis detection to measure transition metals in fossil fuel wastewaters such as O&G brines and CMD waters. Transition metal recovery rates from known standards in DI water matrix and in simple salt matrices were initially evaluated in traditional IC system[25]. Various method parameters such as flow rate, eluent concentration, and sample dilution matrix were optimized for better recovery of transition metals in traditional IC. Later, the CIC system incorporating the CC-1 column for salt removal pre-treatment was introduced. The impact of major ions (e.g., Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, Al^{3+}) on transition metal detection was investigated and reported for the system with and without CIC pretreatment. This study first reports the effectiveness of these alterations and recommends 2% HCl as sample matrix and gradient elution method for optimal transition metal detection. Second, it validates the optimized CIC method using certified materials, and third demonstrates the final metal quantification for CMD and O&G brines collected in the field. This study presents a transition metal detection method by CIC that is cost-effective and fast (18 min per sample) with high salt tolerance that is optimized for and validated by waters from fossil fuel activities.

2. Materials and Methods

2.1 IC-UV/vis system configuration for transition metal detection

This study used an ion chromatograph system (Thermo Scientific Dionex ICS 5000+) with configuration displayed in Figure 1 under operating conditions listed in Table 1. The transition metal detection on IC in this study was optimized from the example application "Determination of trace level of transition metals using CS5A 2-mm column and preconcentration" presented in the CS5A manual, which was the separator column used in this study. This column contains resin with quaternary ammonium functional groups for anion exchange of strongly complexed metals with eluent phase and sulfonic acid groups for cation exchange of free and weakly complexed metals [25].

The tested aqueous sample was injected via an autosampler (Dionex AS-AP) with sample loop of 25 µL onto an on-line chelator column, MetPac CC-1, (See Step 1 in Figure 1). To remove salt matrix, the injection valve first switched to the rinsing mode (See Step 2 in Figure 1) and flushed the CC-1 column with deionized water (DI water, Milli-Q system at 18.2 MΩ· cm) controlled by a Dionex AXP auxiliary pump (1 mL/min, for 7 min). The alkali/alkaline earth cations were rinsed off while the transition metals remained on the CC-1 chelator column. Subsequently, the injection valve switched to injection mode (See Step 3 in Figure 1) and connected the CC-1 column with the eluent stream to deliver the sample to an IonPac CG5A 2x50 mm guard column and CS5A 2x250 mm separator column for separation. All analytes were eluted in approximately 18 min using 18% MetPac PDCA 5x concentrate (35 mM pyridine-2,6-dicarboxylic acid (PDCA), 330 mM KOH, 28 mM K_2SO_4, 370 mM formic acid, hereafter referred to simply as PDCA) and 82% DI water at an isocratic flow rate of 0.3 mL/min. System optimization was conducted later in the study to improve peak resolution in the original method (See Table 1 and Section 2.2).

After individual ions were separated at different retention times, the post-column analytes were mixed with the post column reagent at the "Mixing tee" to form color complexes for subsequent UV-vis detection (See top panel in Figure 1). The post column color agent was prepared by dissolving 4-(2-pyridylazo) resorcinol (PAR) into 1L Dionex MetPac PAR diluent (1.0 M 2-Dimethylaminoethanol, 0.50 M NH_4OH, 0.30 M $NaHCO_3$). The amount of PAR dissolved in the diluent varied depending on the anticipated sample concentration (0.06 g/L for samples with analyte concentrations <0.5 mg/L and 0.12 g/L for analyte concentrations > 0.5 mg/L). The PAR solution changes color from orange to red when complexing with the analytes. The PAR flow rate was controlled by a Dionex PC10 pneumatic pump at 0.15 mL/min. A 375 μL knitted reaction coil provided further mixing for color development of analyte-PAR complexes. The complexes flowed through a Thermo Scientific variable UV/vis wavelength detector (AD40, Dionex) where absorbances at 530 nm were recorded continuously and retention time determined the identity of the analyte. System control and data processing were performed using Chromeleon 7.2 software.

2.2 IC method optimization for transition metals

After installing the MetPac CC-1, the same eluent method (18% PDCA for 18 min) for analyte separation in addition to a 7 min CC-1 cycle was applied in the initial run. However, we noticed some changes to the chromatogram such as a much lower Fe^{3+} peak height and worse separation of peaks from one another especially between $Ni^{2+}$and Zn^{2+} (See supplementary information (SI) Figure S1). We attempted to rectify these changes by altering parameters such as sample matrix (e.g. raw vs 2% HCl vs 2% HNO_3), PDCA eluent concentration, and PDCA eluent flow scheme (isocratic vs. gradient).

To optimize the IC method, mixed transition metal standards containing 2 mg/L Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, and Fe^{2+} were prepared diluted by either DI water, 2% v/v HCl (Fisher Inc., ACS grade), or 2% v/v HNO_3 (Fisher, Inc, trace metal grade) from individual stock solution of 100 mg/L. Individual stock solution of 100 mg/L was prepared by diluting from ICP stock solutions (10,000 mg/L Fe(III) and 1,000 mg/L Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Sigma Aldrich, initially in ≤ 0.1% w/w HNO_3 except for Fe (III) which was in 5% w/w HNO_3. The Fe(II) standards were prepared by creating a 1000 mg/L stock solution by dissolving 0.702 g of ferrous ammonium sulfate (Fisher Inc., ACS grade) in a 100mL solution of 2% v/v HCl and 0.1 M hydroxylamine HCl (a reducing agent to mitigate Fe(II) oxidation by air).

The IC method for transition metals was optimized by adjusting the listed parameters in italics in Table 1. To optimize the sample matrix, each sample (2 mg/L mixed standard) with a different matrix (DI water, 2% v/v HCl, or 2% v/v HNO_3) was measured via the original method (18% PDCA for 18 min) for best recovery of 2 mg/L transition metals. To optimize PDCA eluent concentration, the eluent concentration for IC method setting was varied from 8% PDCA to 48% PDCA in 5% increments while measuring the 2mg/L mixed standard in optimized sample matrix (2% v/v HCl). There were benefits of both higher and lower PDCA concentration, which suggested a gradient elution would be better than isocratic. For instance, lower concentration provided better peak separation, but higher concentration provided better peak symmetry. Peak separation was an issue early in the run for the Ni^{2+} and Zn^{2+} peaks in particular, while peak symmetry was an issue later in the run particularly for Mn^{2+}. Therefore, we further optimized the eluent gradient, two parameters were determined: (1) the time when the gradient increase would begin and (2) the starting and ending concentrations of the gradient. Ultimately a gradient of 17% to 25% PDCA with gradient increase starting at 10 minutes was chosen (See SI Figure S2, dotted line).

2.3 Evaluating salt removal effect for CC-1 column installation

This study also seeks to investigate some of the ion(s) commonly found in fossil fuel wastewaters that interfere with transition metal detection on IC. Different single salts (NaCl

Fisher Scientific ACS Grade, Na_2SO_4 Fisher Scientific 99.8%, $CaCl_2$ EM Science 96%, $AlCl_3$ Sigma Aldrich 99%) at levels of 1000 mg/L or 10,000 mg/L were added to transition metal standard solutions at 5 mg/L in both deionized water and 2% v/v HCl matrix. The ability of the system to accurately measure transition metals in high Na and Ca matrices was assessed before and after the addition of the CC-1 column. Four different samples were prepared by diluting the 100 mg/L stock solution of Co^{2+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} down to 5 mg/L using 1000 or 10,000 mg/L of either NaCl, Na_2SO_4, or $CaCl_2$ as the diluents. Likewise, samples with 5 mg/L of transition metals in 1000mg/L and 10,000mg/L $AlCl_3$ were also prepared, but only for the post CC-1 system. Pre CC-1 measurements were performed once, while post CC-1 measurements were performed in triplicate. Resulting %recovery of pre CC-1 measurements were compared with those of post-CC1 measurements to demonstrate the effect of salt removal on transition metal detection using CIC.

2.4 Sample validation for optimized method and QA/QC

The optimized IC method for transition metals was validated by comparing IC measurements to certified water samples and fossil fuel wastewaters collected from the field. After the method had been re-optimized, two sets of calibration curves were created (1) from 0.0025 mg/L to 1 mg/L for samples expected to have analyte concentrations < 0.5 mg/L and (2) from 0.025 mg/L to 10 mg/L for samples expected to have analytes in concentrations > 0.5 mg/L Two curves were used because Thermo Fisher recommends using higher concentrations (0.12 g/L) of PAR for samples with analyte concentrations above 0.5 mg/L and lower concentrations (0.06 g/L) of PAR for samples with analyte concentrations below 0.5 mg/L.

Quality control during IC runs was maintained by frequent analysis (approximately every 15 samples) of check standards throughout the sample runs. For measurements of samples with concentrations above 0.5 mg/L, a check standard containing 2.5 mg/L of all analytes except Fe^{2+} was used. For those below 0.5 mg/L, a check standard containing 0.25 mg/L of all analytes except Fe^{2+} was used. Fe^{2+} check standards were prepared separately in the same concentrations as the other analytes. All validation and field samples were measured in triplicate.

Six certified water samples were selected for method validation and quality assurance: (1) Initial calibration verification standard 1A (1A, Spexertificate), (2) Trace Metals in Drinking Water Standard (TMDW, High-purity Standards), (3) Certified reference material – seawater (SW, High-purity standards), (4) ground water low (GWL, EnviroMAT), (5) ground water high (GWH, EnviroMAT), and (6) T-231 Standard Reference (T-231, USGS). Resulting IC quantifications (average of triplicates) of transition metals in these samples were compared with certified values.

Wastewater samples from coal, oil and gas industries were provided by the geochemistry team at NETL, including (1) three CMD samples, two from the influent to a treatment system at the Pittsburgh Botanical Garden (PBG) and one from the effluent [7]; (2) two Permian basin produced waters collected from Seminole, TX with names "Permian 1" and "Permian 2" [26]; and (3) three Bakken shale produced waters collected from North Dakota with names "Bakken 1", "Bakken 2", and "Bakken 3" [27]. Wastewater samples were acidified with 2% HCl v/v and stored at 4 °C for long-term prior to use. Prior to IC analysis, all samples were extracted with an acid washed syringe and filtered with acid washed 0.45 μm syringe membranes into IC vials and diluted with 2% v/v HCl if necessary for the established calibration range. Resulting IC quantifications (average of triplicates) of transition metals in these samples were compared with ICP-MS values reported by the Pittsburgh Analytical Lab at NETL.

2.5 Method evaluation metrics

Metrics such as the linearity of the calibration, limits of detection, precision, recovery, peak symmetry, peak width, retention time, etc. were used to evaluate the success of transition metal detection using the developed methods. They can be defined as follows.

2.5.1 Linearity of the Calibration

Linearity of the calibration is the ability of the instrument to maintain a relationship between detector signal and sample concentration that is directly proportional over a given range. It was determined via coefficients of determination (R^2 values) given by the Chromeleon software over the relevant range of concentrations. The relevant calibration range varied for each analyte depending on the highest concentration of analyte present in an unknown sample.

2.5.2 Limits of Detection

In this study, limits of detection was reported as the Hubaux-Vos limit of detection (HV LoD) based on described method in Hubaux and Vos 1970 [28] using a confidence interval of 95% in the Chromeleon software. Specifically, this method asserts that the detection limit is inextricably tied not only to the inherent noise in the instrument but also to arbitrarily chosen upper and lower confidence intervals. For a linear calibration curve, upper and lower confidence intervals run parallel to the curve. These confidence intervals define the likelihood of false positives (often represented as α) and false negatives (often represented as β). A sample whose β equals the blank's α has the concentration of the Hubaux-Vos limit of detection (HV LoD). This is more clearly illustrated in the figures presented in Hubaux and Vos 1970 [31]. Thus the detection limit can be increased or decreased depending on how high a false positive and false negative probability the scientist is willing to accept. Typical confidence intervals are 95% for both upper and lower which means that the probability of false positives and false negatives are both 2.5%.

2.5.3 Precision

Precision is the agreement of multiple measurements compared to each other of the same sample under the same instrument conditions. Precision was assessed by comparing the measurements of a single check standard quantified multiple times throughout the run. The coefficient of variation (CV) was calculated according to equation 1.

$$\%CV = \text{coefficient of variation} = 100 * s/\bar{x} \qquad (1)$$

where s is the standard deviation of a sample set of check standards, and $\bar{x}$ is the mean of the sample set of check standards.

2.5.4 Recovery

Recovery represents the agreement of a measurement with its true value. The recovery of the method was calculated according to equation 2:

$$\%\,recovery = \frac{Measured\ concentration\ of\ analyte}{True\ concentration\ of\ analyte} * 100 \qquad (2)$$

where the true value was either the concentration added via pipette, the certified value, or the value measured by a proven ICP-MS method.

3. Results and Discussion

3.1 Final optimized CIC method vs. pre CC-1 Method from column manual

After optimization, the final method is as follows (Table 2). Many of the parameters remained unchanged from the original method (Table 1). Those in italics were changed from the original method or were entirely new additions to the system (such as inclusion of the MetPac CC-1). The justifications for these changes are presented in the following sections.

3.1.1 Dilution Matrices

Comparison of dilution matrices is illustrated in Figure 2. Based on the resulting chromatographs (Figure 2), 2% HCl was chosen as the sample matrix. Figure 2 shows that using deionized water as the dilution matrix resulted in lower Fe^{3+} peak absorbance. This likely indicates that Fe^{3+} was not fully dissolved and ionized for column surface complexation in the DI water matrix. The figure also demonstrates that DI water yields more overlap of Ni^{2+} and Zn^{2+} peaks compared to the dilute acid matrices. This makes it difficult to determine how much area can be attributed to $Ni^{2+}$and how much to Zn^{2+} for concentration quantification. The chromatographs for samples in 2% HNO_3 and 2% HCl show similar peak shapes and peak absorbance magnitudes except for Fe^{3+} and Fe^{2+}. The Fe^{3+} peak is noticeably larger and the Fe^{2+} peak is noticeably smaller in the 2% HNO_3 sample compared to those in the 2% HCl sample. This can be explained by the fact that HNO_3 is a known oxidant and thus likely oxidized most Fe^{2+} to Fe^{3+} in the aqueous samples. These results demonstrate that samples in 2% HCl matrix should be used over deionized water and 2% HNO_3, especially when analyzing samples with low Fe^{3+} concentrations.

Our study only tested three sample matrices with just two pHs, where the DI water sample has pH of 5.2 and acidified samples have pH of 1.7. The motivation of sample treatment initially was for long-term sample storage, as acidification of water samples was frequently used in water sampling techniques for preservation [29]. Other studies report the effect of pH on the recovery of transition metals using IC methods. Early investigations of IC with pre-concentration using off-line Chelex-100 chelation reported optimum pH range of 5.0-5.5 for transition metal retention and interference removal. This is because the resin appears to reach maximum chelation for transition metals at pH 5.0, below which they will begin to elute, and Ca and Mg experience a local minimum regarding their affinity for the CC-1 between approximately pH 5.0-

5.8 [30,31]. In a subsequent and similar study using the MetPac CC-1, a similar pH range was used [17]. A more recent investigation using the MetPac CC-1 suggested lower optimum chelation ranges of pH 2.8-3.5 for transition metals [21]. Below this range (pH 2.8-2.2), recoveries of Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} appeared to decrease significantly by about 80%. Above this range, a reduction in recovery of Fe^{3+} and Ni^{2+} of approximately 60% and 20%, respectively, occurs [21]. Our data are consistent with Motellier and Pitsch's findings, regarding trends observed above pH 3.5, where we also observed decreased recovery of Fe^{3+} and Ni^{2+} in the sample with DI water matrix at pH 5.2 (See Fig. 2). However, whether acidified samples will decrease the recoveries of Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} peaks remains undetermined since the current study did not include a sample matrix at the optimal pH range of 2.8- 3.5. Future studies are recommended if sample pH needs to be further optimized. Our study decided to use 2% v/v HCl as our optimal sample matrix for later studies, because the peak resolutions and peak heights are satisfactory for detecting transition metals at sub mg/L or mg/L levels in common wastewaters from fossil fuel related fields.

3.1.2 Gradient vs Isocratic Elution

The eluent concentration during the IC run for peak separation was further optimized by testing isocratic elution (one constant concentration of eluent) and gradient elution methods (eluent concentration varies throughout the run). Tests conducted in isocratic PDCA elutions varying from 8% to 48% by 5% increments (selected data in Figure 3A) demonstrate that decreasing concentration of PDCA (from 23% to 13%) led to less symmetrical peaks (particularly Fe, Mn) but better separation from each other as indicated visually by the chromatographs. Therefore, there are trade-offs to both high PDCA and low PDCA concentrations. A gradient elution was implemented to take advantage of the benefits of both high and low PDCA concentrations. By comparing various isocratic methods and gradients methods (Figure 3B), the gradient method was selected with a run time of just 18 min. In detail for the final gradient method, the initial concentration of PDCA was decreased slightly from 18% (in the original method) to 17% and then increased to 25% right after the elution of nickel to reduce broadening and improve symmetry of the Mn^{2+} peak. Most studies investigating the use of the MetPac CC-1 have used isocratic 6 mM PDCA [8,17,19–22] or 7 mM PDCA [23,32,33] elution (equivalent of 17% to 20% PDCA isocratic method discussed here).

3.2 **Salt removal effect before and after CC-1 column installation**

Table 3 displays the recoveries of samples with additional NaCl, $CaCl_2$ and Na_2SO_4 at levels of either 1000 mg/L or 10,000 mg/L before and after the CC-1 installation for salt removal. The post CC-1 samples were not acidified here so that they could be directly compared to the pre CC-1 recovery, which were also not acidified. Post CC-1 recoveries with 2% HCl are presented in Table S1.

Before the CC-1 column was installed, additional NaCl (up to 10,000mg/L) appears to have little effect on %recoveries of different transition metals (97.0% - 104%). Our results suggest that the high NaCl present in most O&G produced waters may not interfere with transition metal IC detection. As an exception, our results show that the presence of 10,000 mg/L Na_2SO_4 likely decreases the recovery of Fe peak on IC (84.1% recovery). Using Minteq geochemical software, under current analysis conditions (2% HCl 100 mg/L stock solutions diluted to 5 mg/L standard using 10,000mg/L Na_2SO_4 as diluent), there is no precipitation predicted in the model. Noticeably, 83.4% of Fe exists as $Fe(SO_4)_2^-$, whereas other transition metals mainly exist (>99%) as cations or neutrally charged aqueous phases (Table S2). For example, Cu species exist as 68.2% Cu^{2+}, 4.83% $CuCl^+$, and 24.9% $CuSO_4$(aq). This iron sulfate anionic complex $Fe(SO_4)_2^-$ in high sulfate solutions could be the possible cause of decreased Fe recovery using the current IC column. According to the Dionex Technical Note 10, the anionic complexes with a net negative charge, like $Fe(SO_4)_2^-$, will not likely be displaced during chromatography, when the current method with CS5A column in PDCA eluent mainly targets hydrated and weakly complexed metal cations [34]. Metal oxyanions (e.g., $Fe(SO_4)_2^-$) and other stable metal complexes will usually need anion-based IC system for determination.

Table 3 demonstrates that the presence of 10,000 mg/L $CaCl_2$ impacted recoveries of multiple transition metals significantly before CC-1 was installed (recovery rates as 147% for Fe^{3+}, 323% for Cu^{2+}, 137% for Zn^{2+}, 43.4% for Co^{2+}, and 1.89% for Mn^{2+}). High Ca in the sample matrix has been reported to form complexes with PDCA which can interfere with anion exchange between transition metal PDCA complexes and the CS5A resin. Mn is particularly affected because it has the lowest affinity for the CS5A column among the tested metals [21].

The data in bold in Table 3 demonstrates overall improvement of recovery rates after CC-1 installation, indicating salt removal using CC-1. Noticeably, the recovery rates of transition metals in 10,000 mg/L $CaCl_2$ significantly improved upon CC-1 installation from 1.89-323% recoveries for pre CC-1 transition metals to 87.0-108% for post CC-1 transition metals.

Calcium is the most problematic interfering ion tested in this study even after CC-1 installation (overall recoveries of 87.0-108%), compared to Na^+, Cl^- or SO_4^{2-} (overall recoveries of 97.0%-103%). This may be attributed to Ca having the highest affinity for the CC-1 resin compared to other alkali, alkaline earth cations such as Na, Mg, and K [20, 23]. Thus, although Mg and K were not tested in this study, we anticipate that their influence on detection will not be as great as Ca because their affinity for the CC-1 is not as high [18]. Figure 4 shows that the analytes gain retention time and a broad peak begins to form prior to Fe^{3+} in the presence of high

$CaCl_2$ even after CC-1 installation. This could be due to the formation of Ca[PDCA] complexes which can compete for anion exchange sites with transition metals. Our results agreed with other studies, where high levels of calcium were found to compromise transition metal recovery [10,17,21,33]. Motellier and Pitsch (1996) demonstrated very similar results to Figure 4 with CC-1 installed, showing a Ca^{2+} peak just before Fe^{3+}, retention time shift, and preferential decrease in peak height for Mn^{2+} compared to other transition metals [21]. These influences are not observed in the chromatographs for NaCl, Na_2SO_4, or $AlCl_3$ which are shown in figures S3, S4, and S5 respectively.

The recovery of Mn^{2+} peak is significantly impacted by excessive presence of Ca^{2+}. Cardellicchio et al. (1999) discussed that the presence of Ca^{2+} and Mg^{2+} at levels of approximately 100-500 times greater than transition metals will incur noticeable peak height decrease in IC chromatography [33]. Siriraks et al. (1990) corroborated this finding and found a significant decrease in Mn^{2+} with only 23% recovery in a solution with 0.1% Ca^{2+} [17]. This can be attributed to Ca^{2+} competing with Mn^{2+} for sites on the CC-1 and forming complexes with PDCA, leaving less PDCA to complex with the transition metals. This competition occurs particularly between Mn^{2+} and Ca^{2+}, when Mn^{2+} forms the weakest PDCA complex of the tested metals. Consequently, the installation of the CC-1 column greatly improved the calcium tolerance for transition metal detection. With the CC-1, the data presented here as well as that from Motellier and Pitsch demonstrate recoveries of at least 80% in solutions containing Ca^{2+} of 1,000 to at least 10,000 times greater than transition metals [21]. This increased salt tolerance would give the IC the ability to measure transition metals in matrices such as seawater and brines, which has been demonstrated in prior studies [19].

3.3 Data Validations

3.3.1 Calibration Statistics

Prior to running certificate and field samples for validation, two sets of calibration curves were created (Table 4). Linearity of the calibration for each element represented by R^2 coefficients was greater than 0.99 for most elements (Table 4). Limits of detection as calculated by the Hubaux-Vos method were approximately within the range of 0.0109 to 0.161 mg/L (10.9 – 161 μg/L). The limits of detection in this study (10.9 – 161.2 μg/L) were comparable to a previous method with a similar sample loop of 25 μL, where detection limits in the range of 0.006 to 0.056 mg/L (6-56 μg/L) were reported [8]. Other studies were able to achieve detection limits in the ng/L range using larger sample loops (up to 50 mL) [17,22,30]. Such loops allow for a greater mass of analytes to be loaded onto the column prior to separation and detection, which improves sensitivity.

The check standard coefficient of variation (CV) was under 10% for all analytes except Ni^{2+} for the 0.0025-1.0 mg/L calibration curve. Ni^{2+} peak is usually the shoulder peak on the bigger Zn^{2+} peak, which explains more peak area variations compared to other large and independent peaks on the chromatographs (Figures 2, 3 and 4). In addition, in the 0.0025-1.0 mg/L calibration curve, only three different check standards were analyzed (Table S3), allowing variations in any one sample to have a large impact on the overall mean and standard deviation. This could explain the high coefficient of variation for Ni^{2+}.

Fe^{2+} can only be quantified at the high end of the calibration range of 0.025 – 10 mg/L with a R^2 of 0.987 and LoD of 2.35 mg/L (Table 4). The reduced performance could be due to (1) possible Fe^{2+} oxidation during or before the IC run and (2) the relatively weak affinity of Fe^{2+} to an iminodiacetate resin [35]. Nonetheless, we still used the Fe^{2+} calibration for the iron quantification in the Bakken shale samples, where iron was mostly in the form of Fe^{2+} and was well above the detection limit of 2.35 mg/L.

3.3.2 Validation by Certified Samples

Recovery of the method was generally better for the samples with transition metals at mg/L levels, compared to those at sub mg/L levels. Table 5 shows the data comparing the average values measured by the IC method with the certificate values for tested certified samples. For instance, certified samples 1A and GWH, which each contained analytes at least four times greater than the detection limit, were each measured within about 10% of the certified value for all analytes. On the other hand, samples with values closer to the detection limit were generally less accurate. For instance, GWL, SW, and TMDW contained analytes within five times or below the detection limit. At these levels, it becomes more difficult to distinguish a legitimate peak from the baseline. This could be remedied by increasing the size of the sample loop (up to 50 mL) and thereby adding more mass to the column, which would lower detection limits. Larger sample loops have been applied successfully in many studies with this system resulting in detection limits multiple orders of magnitude lower [8,10,11,19,21,23,32].

3.3.3 Field Samples

Quantification values from current IC methods and ICP-MS are presented in Table 6. PBG CMD samples (PBG 2018 influent, PBG 2019 influent and PBG 2019 effluent) were generally more accurate than O&G wastewater samples (Bakken 1-3, Permian 1,2). Total recoveries of all elements for CMD samples are between 72.4% - 122%, except for Zn^{2+} (2% - 35%). This could be due to most of the Zn being present in species other than Zn^{2+} that are not detectable by IC. The Zn colloids, such as Zn sorbed Fe oxyhydroxides, were reported to be the most important species for trace metal transport in acid mine drainage systems, but the colloidal species cannot be detected by IC method [36–38].

Oil and gas wastewater samples had poor recoveries due to their higher salt content compared to CMD samples (See major elemental compositions in Table S4). The O&G wastewater samples contained high levels of Ca (> 1,750 mg/L) according to ICP-MS measurements, with the Bakken shale samples containing Ca concentrations greater than 17,000 mg/L (Table S4). These high levels of Ca could explain the consistent underreporting of Mn^{2+} concentrations (17.0% - 84.7% recoveries) for these samples. Mn^{2+} was not underreported for CMD samples (102% - 105% recoveries), which contained only about 100 mg/L Ca (Table S4). Furthermore, a broad Ca peak can be seen in the chromatograms similar to or worse than the Ca peaks shown earlier in Figure 4. These Ca peaks are illustrated in Figures S6 and S7 for two samples (Bakken 3 and Permian 2).

The detectable analytes measured in Bakken shale produced water samples were within $\pm$40% of ICP-MS values (72.3% - 138% recoveries), whereas the Permian basin samples (EMMA A and ESSAU 50) were less accurate. This is probably because: (1) the analytes in Permian basin samples were closer to the detection limit. (2) the Permian basin produced waters generally have higher ratios of Ca to analytes compared to Bakken shale produced waters (Table S5). As discussed in section 3.2, higher Ca to analyte ratios will result in inefficient analyte recoveries using the current IC method. Especially when this ratio is above 10,000 and expected analyte concentrations are very low, the CC-1 column might not remove enough Ca for effective transition metal detection. There are 5 out of 15 analytes in Bakken shale samples and 8 out of 10 analytes in Permian basin samples that exceed Ca to analyte ratio of 10,000 (Table S5). Therefore, accurate IC detection of these analytes in O&G produced waters might be difficult, especially for produced waters with high Ca to transition metal ratios. Nonetheless, the current IC method can still be a very good screening tool for fast and cheap analysis for transition metals at mg/L level, to facilitate selection of samples for more detailed ICP-MS analysis.

4. Conclusions

A method was developed for the quantification of transition metals in high salt matrices, particularly those originating from fossil fuel wastewaters such as CMD and O&G wastewaters. The MetPac CC-1 column enables online removal of interfering alkali and alkaline earth metals through the process of chelation ion chromatography. Tests on sample dilution matrices indicate that addition of low concentrations of hydrochloric acid is beneficial for transition metal quantification using IC. In particular, Fe^{3+} quantification will be greatly improved by using 2% HCl matrix instead of DI water or 2% HNO_3. Gradient elution (17% - 25% PDCA in 18 min) is more adaptable than isocratic elution, as slight improvement on nickel-zinc peak separation and Mn peak symmetry was found in gradient eluent method.

Current method with CC-1 column showed great tolerance of salts in the presence of 10,000mg/L NaCl, Na_2SO_4 and $CaCl_2$ (overall recoveries of 93% - 108%), except for reduced recovery of Mn (87%) in the presence of 10,000 mg/L $CaCl_2$. This can be attributed to cation exchange between Ca^{2+} and Mn^{2+} as well as Ca^{2+} forming complexes with PDCA leaving less PDCA to complex with the transition metals. Future research could seek to optimize the CC-1 rinse solution to further improve Ca removal.

The detection limits of this method were 10.9 – 161 μg for various transition metals, comparable to IC methods using a similar sample loop volume (25 μL). A larger sample loop volume can further improve detection limits to ng/L. The method was generally in agreement with certificate samples used for validation, including drinking water, groundwater and seawaters, except for those analytes near the detection limits from this method. IC results for CMD samples and O&G produced water samples were in good agreement with reported ICP-MS values (mostly within 30% error), except for selected O&G samples with high Ca to transition metal ratio (e.g., Permian basin produced waters). Our study has presented a successful analytical method with high salt tolerance to detect sub mg/L level transition metals from fossil fuel related waters. The method still has recovery limitations for water samples with high Ca to transition metal ratio (> 10,000), which will require additional research. Nonetheless, the current IC method is an effective screening tool for fast and inexpensive analysis for transition metals at mg/L level, to facilitate selection of samples for more detailed ICP-MS analysis.

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Figure Captions:

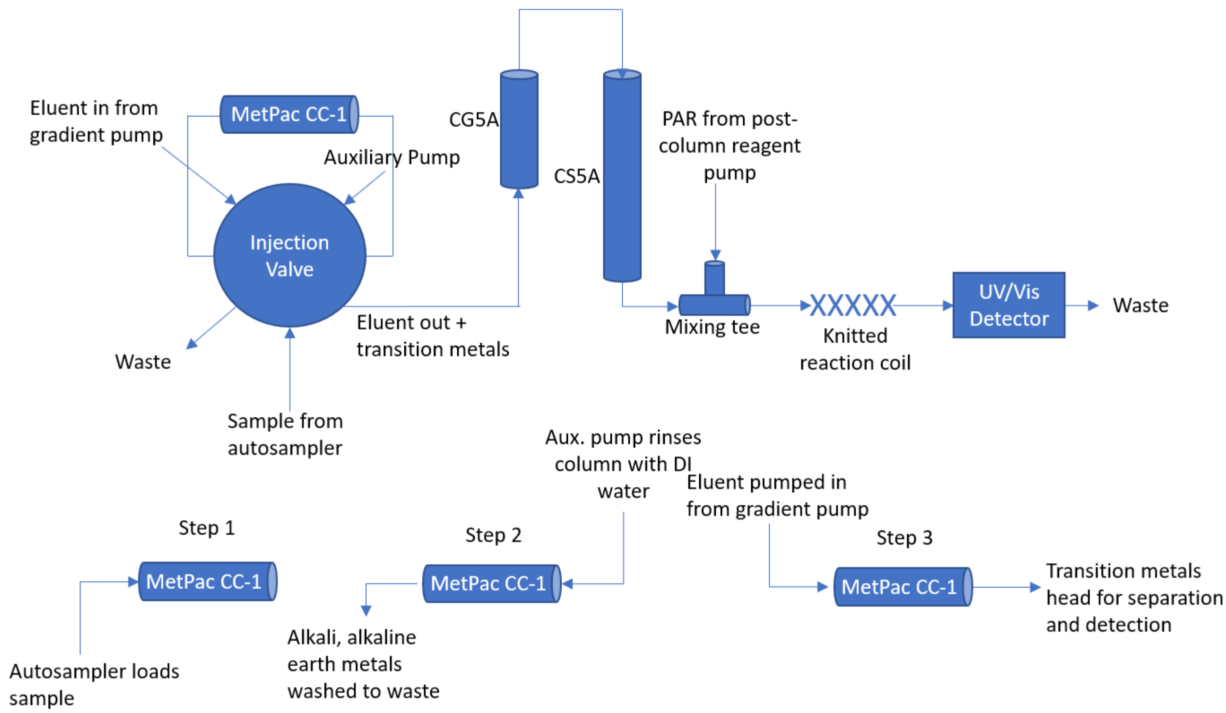
Figure 1. Diagram of IC-UV/vis system configuration for transition metal detection. Top – full-system diagram. Bottom – Diagram showing operation of chelator column mediated by the injection valve.

Figure 2. Comparison of chromatographs with different dilution matrices. All contained 2 mg/L of each analyte (Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, and Fe^{2+}), but each had a different dilution matrix. One sample was diluted in 2% nitric acid (green), one sample in 2% hydrochloric acid (orange), and one sample in deionized water (blue).

Figure 3. (A) Comparison of elution under high PDCA concentration (23% blue) vs low PDCA concentration (13% orange). Sample contained 2 mg/L Fe^{3+} (1), Cu^{2+} (2), Ni^{2+} (3), Zn^{2+} (4), Co^{2+} (5), Mn^{2+} (6), and Fe^{2+} (7). (B) Comparison of isocratic elution at 17% (blue), isocratic elution at 18% (orange), and gradient elution from 17% to 25% (green). Samples were 2.5 mg/L of Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, and Mn^{2+} in 2% HCl.

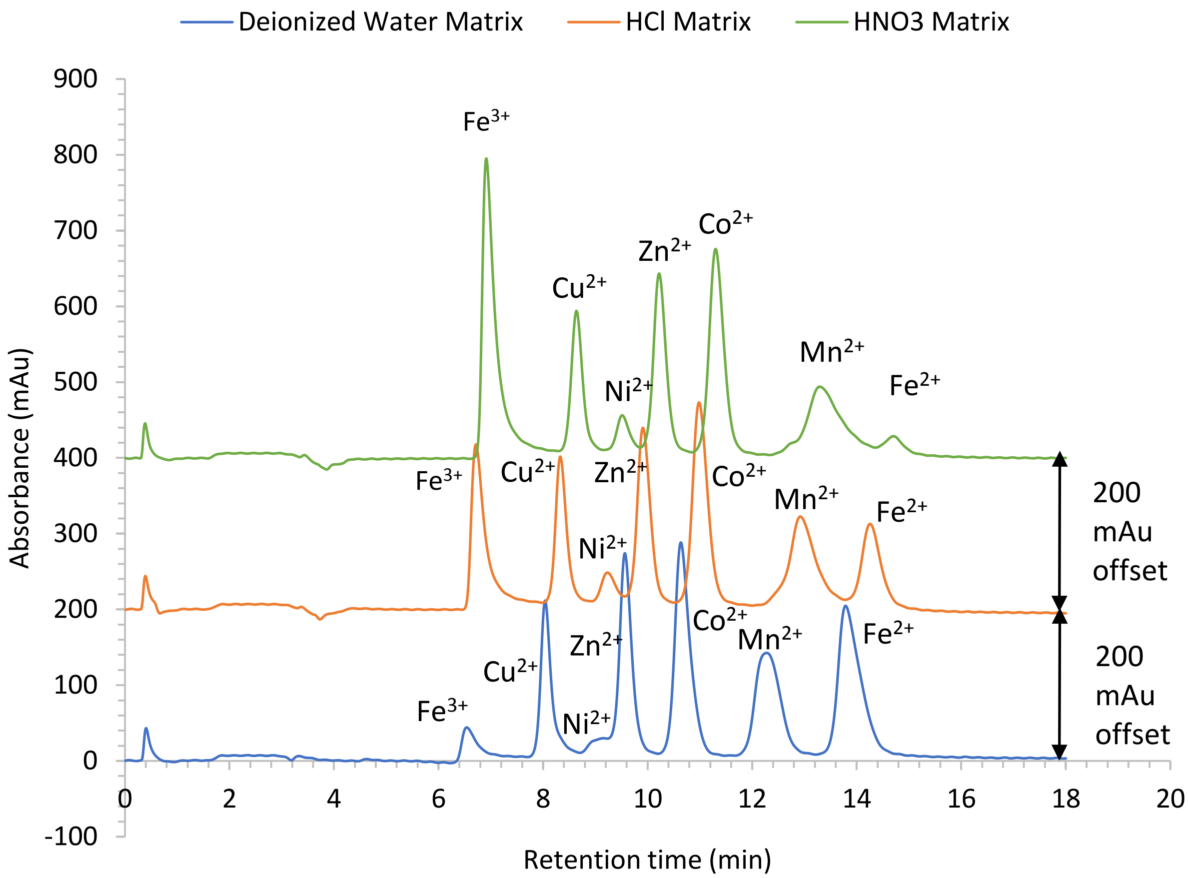
Figure 4. Comparison of chromatograms in matrices of increasing calcium concentration after CC-1 installation: DI water (blue), 1,000 mg/L $CaCl_2$ (orange), and 10,000 mg/L $CaCl_2$ (green). Samples contained 5 mg/L Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, and Mn^{2+}.

Figure 1



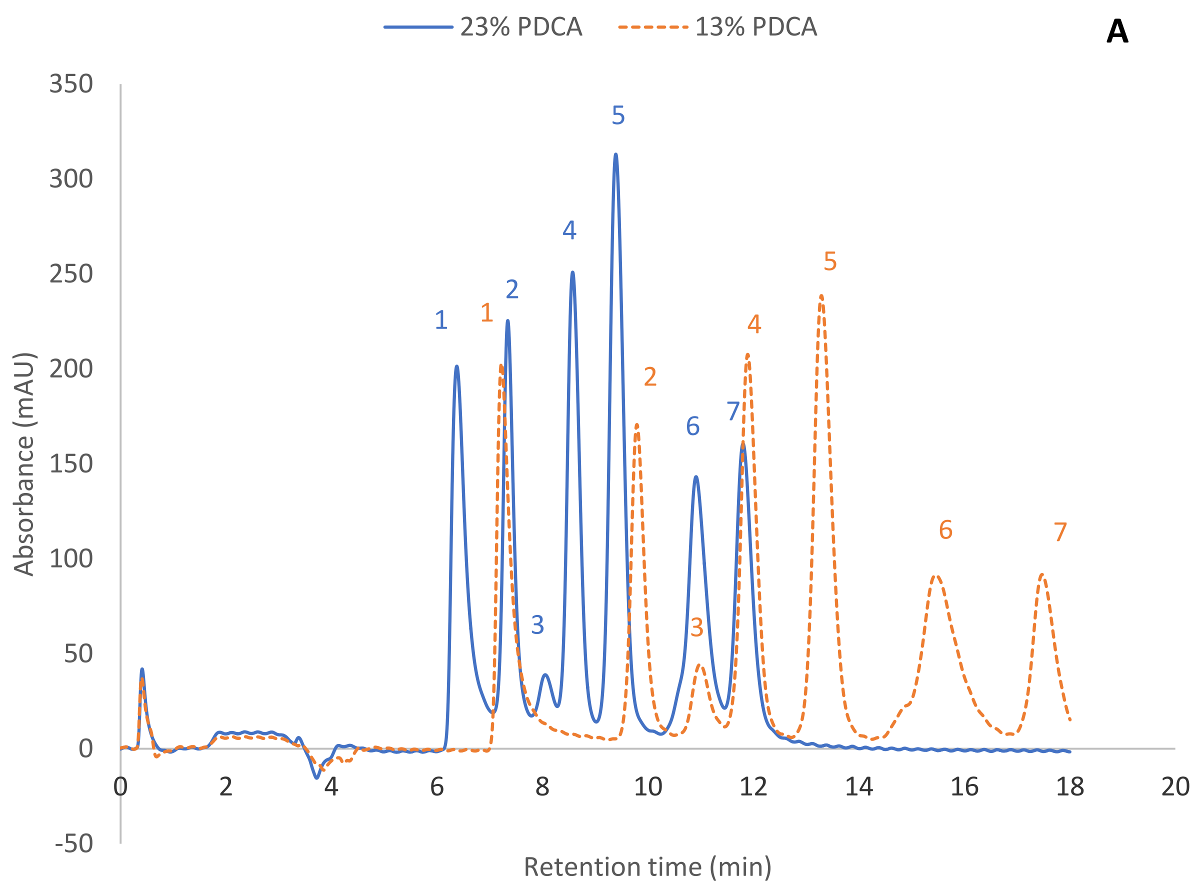
Eluent in from gradient pump
MetPac CC-1
Auxiliary Pump
Injection Valve
Waste
Sample from autosampler
Eluent out + transition metals
CG5A
CS5A
PAR from post-column reagent pump
Mixing tee
XXXXX
Knitted reaction coil
UV/Vis Detector
Waste
Step 1
MetPac CC-1
Autosampler loads sample
Step 2
MetPac CC-1
Aux. pump rinses column with DI water
Alkali, alkaline earth metals washed to waste
Eluent pumped in from gradient pump
Step 3
MetPac CC-1
Transition metals head for separation and detection

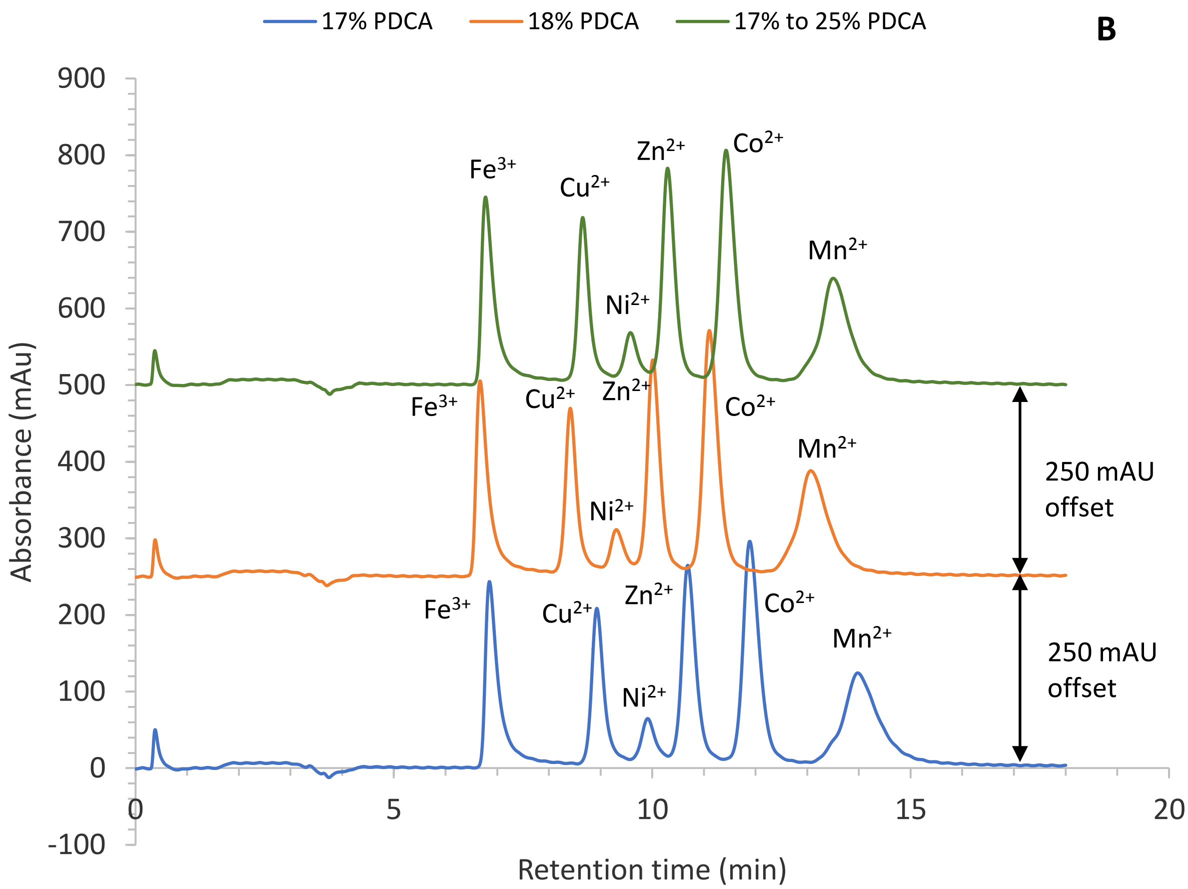
Figure 2



Deionized Water Matrix
HCl Matrix
HNO3 Matrix
Absorbance (mAu)
Retention time (min)
Fe^{3+}
Cu^{2+}
Ni^{2+}
Zn^{2+}
Co^{2+}
Mn^{2+}
Fe^{2+}
200 mAu offset
200 mAu offset

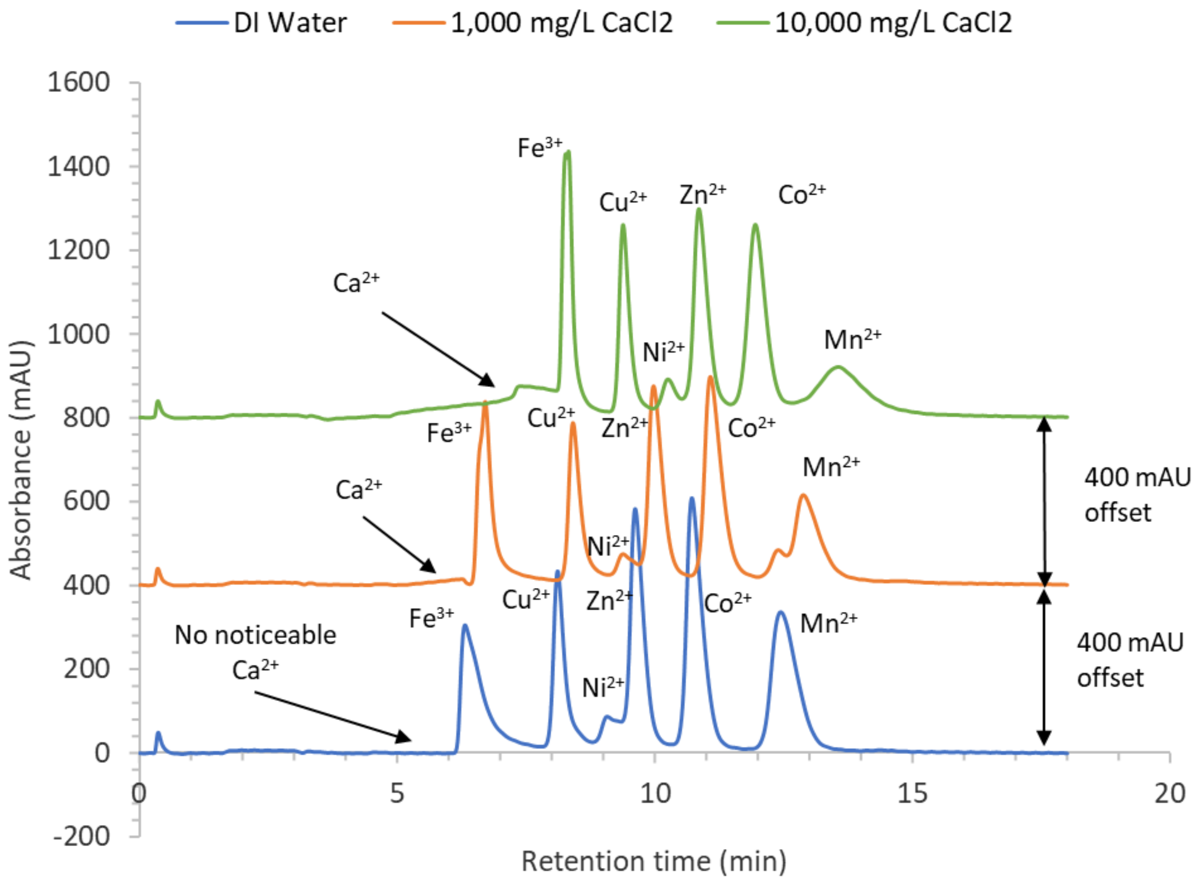
Figure 3


23% PDCA
13% PDCA
A
Absorbance (mAU)
350
300
250
200
150
100
50
0
-50
0
2
4
6
8
10
12
14
16
18
20
Retention time (min)
1
2
3
4
5
6
7
1
2
3
4
5
6
7



17% PDCA
18% PDCA
17% to 25% PDCA
B
900
800
700
600
500
400
300
200
100
0
-100
Absorbance (mAu)
0
5
10
15
20
Retention time (min)
Fe3+
Cu2+
Ni2+
Zn2+
Co2+
Mn2+
250 mAU offset
250 mAU offset

Figure 4



DI Water
1,000 mg/L CaCl2
10,000 mg/L CaCl2
1600
1400
1200
1000
800
600
400
200
0
-200
Absorbance (mAU)
0
5
10
15
20
Retention time (min)
Fe3+
Cu2+
Zn2+
Co2+
Ca2+
Ni2+
Mn2+
Fe3+
Cu2+
Zn2+
Co2+
Ca2+
Ni2+
Mn2+
400 mAU offset
Fe3+
Cu2+
Zn2+
Co2+
No noticeable Ca2+
Ni2+
Mn2+
400 mAU offset

Table 1. IC method conditions. Parameters in italics were tested for optimization.

Parameter	Conditions
Column	2-mm IonPac CG5A Guard and 2-mm CS5A Analytical Column
Eluent Composition	MetPac PDCA 5x concentrate and DI water mix via gradient pump
Eluent flow rate	0.3 mL/min
Back pressure	1800 psi
Post-column agent	0.12 g PAR/1L MetPac post-column diluent (0.5mM)
Post-column flow rate	0.15 mL/min
Injection volume	25 µL
Detection	absorbance at 530 nm
Column Temperature	30 °C
Sample matrix	*raw vs. 2% HNO_3 vs. 2% HCl*
Eluent gradient	*Isocratic (18% PDCA concentrate) vs. gradient (various PDCA)*
Chelation Column	*Pre- vs. post-MetPac CC-1*
Auxiliary rinse cycle	*None vs. 7 min*

Table 2. Final optimized CIC Conditions

Parameter	**Conditions**
Column	2-mm IonPac CG5A Guard and 2-mm CS5A Analytical Column
Eluent Composition	MetPac PDCA 5x concentrate and DI water mix via gradient pump
Eluent flow rate	0.3 mL/min
Back pressure	1800 psi
Post-column agent	0.12 g PAR/1L MetPac post-column diluent (0.5mM) for samples > 0.5 mg/L; 0.06 g PAR/1 L for samples <0.5 mg/L
Post-column flow rate	0.15 mL/min
Injection volume	25 µL
Detection	absorbance at 530 nm
Column Temperature	30 °C
Back pressure	1800 psi
Sample matrix	*2% v/v HCl*
Eluent gradient	*Gradient elution: CC-1 rinse from -7-0 min, 17% 5x PDCA Concentrate from 0-10 min, 10-14 min increasing from 17% to 25% PDCA, 14-17.9 min 25% PDCA, 17.9-18 min decreasing from 25% to 17%.*
Chelation Column	*MetPac CC-1*
Concentrator cycle	*8 min*

Table 3. %Recovery of transition metal measurements for 5 mg/L transition metal mixed standard before and after incorporation of CC-1 in various salt solutions. $\%Recovery = \frac{concentration\ measured\ by\ IC}{Expected\ concentrations} * 100$, where expected concentration for each analyte is 5 mg/L

Values in italics indicate %recovery is out of 90% - 105% range. Values in bold indicate improvement of %recovery after CC-1 installation.

Salt addition	**CC-1 installed**	**Fe^{3+}**	**Cu^{2+}**	**Ni^{2+}**	**Zn^{2+}**	**Co^{2+}**	**Mn^{2+}**
1000 mg/L NaCl	Pre	103	100	100	103	103	101
1000 mg/L NaCl	Post	**98.5**	101	100	**102**	**101**	101
10,000 mg/L NaCl	Pre	104	97.8	97.0	103	104	103
10,000 mg/L NaCl	Post	**98.9**	**101**	93.7	**102**	**101**	**100**
1000 mg/L Na_2SO_4	Pre	102	97.8	94.6	102	103	102
1000 mg/L Na_2SO_4	Post	**99.4**	**102**	**97.2**	102	**101**	**101**
10,000 mg/L Na_2SO_4	Pre	*84.1*	101	105	107	106	104
10,000 mg/L Na_2SO_4	Post	**102**	**102**	92.9	**103**	**102**	**102**
1000 mg/L $CaCl_2$	Pre	105	101	101	104	105	106
1000 mg/L $CaCl_2$	Post	**95.7**	92.7	92.2*	96.0	**95.7**	**100**
10,000 mg/L $CaCl_2$	Pre	*147*	98.5	*323*	*137*	*43.4*	*1.89*
10,000 mg/L $CaCl_2$	Post	**98.1**	93.0	**108***	**101**	**95.0**	***87.0***

*: Most % recovery rates for post CC-1 tests are calculated from average values of triplicate measurements on IC with relative standard deviation (RSD) less than 4%. Values in * have a RSD > 4%.

Table 4. Calibration statistics. Linearity as determined by R^2 coefficients, limits of detection as determined by the Hubaux and Vos Method [31] and precision as determined by the coefficient of variation of check standards.

Calibration Range	**0.0025-1 mg/L**			**0.025-10 mg/L**		
	R^2	**LoD (mg/L)[b]**	**CV[a]**	**R^2**	**LoD (mg/L)[b]**	**CV[a]**
Fe^{3+}	0.99997	0.0109	2.14%	0.99990	0.161	4.71%
Cu^{2+}	0.99927	0.0279	3.11%	0.99997	0.0898	1.57%
Ni^{2+}	0.99425	0.0706	17.1%	0.99998	0.0838	7.86%
Zn^{2+}	0.99976	0.0167	1.52%	0.99995	0.113	2.36%
Co^{2+}	0.99922	0.0289	5.00%	0.99999	0.0549	1.50%
Mn^{2+}	0.99997	0.0110	3.36%	0.99999	0.0465	5.46%
Fe^{2+}	N/A	N/A		0.98707	2.35	

[a]CV = Coefficient of variation

[b]Hubaux-Vos limit of detection

Table 5. Recovery of IC method as compared to certificate standards. All samples were diluted in 2% HCl and all measurements are the average of triplicates. ND = not detectable

	Units	**Fe^{3+}**	**Cu^{2+}**	**Ni^{2+}**	**Zn^{2+}**	**Co^{2+}**	**Mn^{2+}**
Hubaux-Vos Detection Limit	mg/L	0.0109	0.0279	0.0706	0.0167	0.0289	0.0110
1A – IC	mg/L	106	27.0	38.5	20.5	52.9	14.2
1A- Cert.	mg/L	98.5	24.7	39.4	19.8	49.4	14.8
1A – Recovery		108%	110%	97.7%	103%	107%	95.8%
GWH – IC	mg/L	1.30	0.839	0.838	0.836	0.129	0.337
GWH – Cert.	mg/L	1.29	0.800	0.840	0.881	0.128	0.345
GWH – Recovery		101%	99.4%	99.7%	94.9%	101%	97.7%
GWL – IC	mg/L	0.0306[a]	0.00890[ab]	ND	0.0106[b]	0.0181[ab]	0.0375
GWL – Cert.	mg/L	0.0110	0.00900	0.00400	0.0110	0.0200	0.0400
GWL – Recovery		281%	95.2%	ND	101%	91.9%	94.7%
SW – IC	mg/L	0.0408	0.00980[b]	ND	0.0100[b]	ND	0.0239
SW – Cert.	mg/kg	0.0200	0.0100	0.000100	0.00500	NA	0.0100
SW – Recovery		204%	98.0%	ND	200%	ND	239%
TMDW – IC	mg/L	0.115	0.0149[b]	0.0500[b]	0.0593	0.0216[ab]	0.0324
TMDW – Cert.	mg/L	0.100	0.0200	0.0600	0.0700	0.0250	0.0400
TMDW – Recovery		115%	74.5%	83.3%	84.7%	86.4%	81.0%
T231 - IC	mg/L	0.220	0.00660[b]	ND	0.165	ND	0.0260
T231 – Cert.	mg/L	0.253	0.00600	0.00100	0.185	0.00200	0.0280
T231 – Recovery		87.0%	103%	ND	89.4%	ND	91.6%

[a]RSD > 10%

[b]Below Hubaux-Vos detection limit

Table 6. Recovery of IC for Field Samples Compared to ICP-MS. ND: analyte peaks not detectable on IC chromatography. BDL: below detection limit of ICP-MS. N/A: not applicable in ICP-MS method to detect Fe^{3+} and Fe^{2+}. Only Fe total is reported for ICP-MS.

	Fe^{3+}	**Cu^{2+}**	**Ni^{2+}**	**Zn^{2+}**	**Co^{2+}**	**Mn^{2+}**	**Fe^{2+}**	**Fe total**
PBG 2018 Influent - IC	0.5632	0.0162[a]	0.0921	0.139	0.0510	0.545	ND	0.563
PBG 2018 Influent - ICP-MS	N/A	0.0164	0.127	4.21	0.0511	0.534	N/A	0.462
PBG 2018 Influent - Recovery		98.8%	72.4%	3.29%	100%	102%		122%
PBG 2019 Influent - IC	0.368	0.0126[a]	0.110[a]	0.118	0.0412	0.499	ND	0.368
PBG 2019 Influent - ICP-MS	N/A	0.0126	0.105	6.53	0.0406	0.475	N/A	0.301
PBG 2019 Influent - Recovery		99%	106%	1.81%	102%	105%		122%
PBG 2019 Effluent - IC	0.180	ND	0.0616	0.126	0.0137	0.191	ND	0.180
PBG 2019 Effluent - ICP-MS	N/A	0.00125	0.0605	0.362	0.0157	0.187	N/A	BDL
PBG 2019 Effluent Recovery		ND	102%	34.7%	87.3%	102%		BDL
Bakken 1 - IC	7.47[a]	ND	ND	ND	ND	9.00	67.7	75.2
Bakken 1 - ICP-MS	N/A	0.412	BDL	BDL	BDL	12.5	N/A	63.1
Bakken 1 - Recovery	119%	ND	ND	ND	ND	72.3%		107%
Bakken 2 - IC	46.5	ND	ND	24.8	ND	23.0	455	501
Bakken 2 - ICP-MS	N/A	0.455	0.120	21.1	BDL	27.1	N/A	375
Bakken 2 - Recovery		ND	ND	117%	ND	84.7%		134%
Bakken 3 - IC	30.5	ND	ND	40.3	ND	81.6	243	274
Bakken 3 - ICP-MS	N/A	0.577	0.369	39.1	BDL	110	N/A	199
Bakken 3 - Recovery[b]		ND	ND	103%	ND	74.1%		138%
Permian 1 - IC	0.121[a]	0.0446[a]	ND	0.0197	ND	ND	ND	0.121

Permian 1 - ICP-MS	N/A	0.0284	<DL	<DL	0.000738	0.141	N/A	0.360
Permian 1 - Recovery		157%	ND	ND	ND	ND		33.5%
Permian 2 - IC	0.2468[a]	0.0356[a]	ND	ND	ND	0.0271[a]	ND	0.247
Permian 2 - ICP-MS	N/A	0.0970	0.0175	<DL	0.00368	0.159	N/A	0.123
Permian 2 - Recovery		36.7%	ND	ND	ND	17.0%		201%

[a]RSD > 10%

[b]Measured in duplicate instead of triplicate