



METHOD DEVELOPMENT FOR PRECONCENTRATION AND QUANTIFICATION OF CRITICAL ELEMENTS IN PERMIAN BASIN PRODUCED WATERS

PIONEER
NATURAL RESOURCES

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Fig. 1



Fig. 3



Fig. 4



Fig. 5



Fig. 6

Purpose of Study/Background:

The purpose of our study is to determine methods to quantify critical and valuable elements (CVE) in Permian Basin produced waters through ion-exchange preconcentration and purification. In particular the effects of produced water composition and salinity were investigated.

We modified the method of Zhu et al. (2005) who utilized Chelex-100 (iminodiacetic acid) packed minicolumns to preconcentrate trace metals in seawater followed by analysis via inductively coupled plasma-mass spectrometry (ICP-MS). The method includes removal of matrix ions by washing the loaded resin with a 1 molar ammonium acetate ($\text{NH}_4\text{CH}_3\text{COO}$) solution followed by ultrapure water. Elements were eluted from the resin using a small volume of 2 molar nitric acid. Their study revealed that the optimal pH for recoveries of rare earth elements (REEs) and transition metals is circa 6.0. Several oxyanions and high field strength elements (Mo, Sn, Ti, V and W) exhibited near complete recovery closer to pH 4. However, their method did not examine recovery for solutions more saline than seawater or consider the impact of variable Na/Ca ratios.

Produced waters from the Permian Basin often exceed the salinity of seawater (35 g/L), with maximum values of over 400 g/L. Zhu et al.'s study stated that matrix elements (salts) can cause instrumental drift, isobaric polyatomic interferences and signal suppression when determining trace metal concentrations using ICP-MS, making this a variable which must be considered before analyses. Moreover, Although being dominated by just 3 ions (Ca, Cl, and Na) produced waters exhibit a significant variation in Na/Ca ratios when compared to seawater. Our study aims to bridge this gap of knowledge and provide reliable data quantifying CVE concentrations in produced waters of the Permian Basin.

Column Chemistry Procedure:

- 50 mL sample solutions were adjusted to a pH of 6 using ultrapure NH_4OH and/or HCl. pH was monitored using Sper Scientific Benchtop pH-mV meter (Fig. 1).
- 0.25 ml of pre-treated Chelex-100 resin slurry stored in 1 molar $\text{NH}_4\text{CH}_3\text{CO}_2$ solution (pH adjusted to 6) was packed into mini columns with pipettor (Fig. 2).
- 50 ml solutions were loaded onto resin in 60 ml BD syringes at a flowrate of 3 ml/min using a Braintree Scientific BS-9000-8 Multi syringe pump (Fig. 3).
- Sample matrix elements are removed successively from the resin with 8 ml of 1 molar ultrapure $\text{NH}_4\text{CH}_3\text{COO}$ and 5 ml of 18.2 M Ω /cm water at a flow rate of 2 ml/min. (Fig. 4).
- Elements of interest are eluted from the Chelex 100 resin using 4 ml of 2 molar ultrapure HNO_3 pumped at a flow rate of 0.5 ml/min. (Fig. 5).
- The eluted sample was then dried down at 65°C in a class 100 laminar flow hood and brought up to 5 ml using 2% ultra pure HNO_3 , concentrating the sample by a factor of 10.
- Element concentrations were determined using a Thermo Scientific iCAP-Q-ICP-MS (Fig. 6) using the KED (collision cell) mode. The system was run in collision cell mode to minimize the effects of polyatomic species. ¹¹⁵Indium was used as an internal standard to improve the stability and performance of the instrument.

Preliminary Research:

Impact of Ca and Na: To determine the uptake of Na and Ca in brines by the Chelex 100 resin and to ensure that the eluted solution salinity was low enough to be run directly via ICP-MS (<500 mg/L), Ca-rich (Na/Ca molar ratio of 5) and Na-rich (Na/Ca molar ratio of 50) solutions of total dissolved solids of 50-300 g/L were run through the column chemistry and concentrations of Na and Ca in the eluted samples were quantified via inductively coupled plasma-optical emission spectrometry (ICP-OES).

Initial element recovery: Na-rich (Na/Ca molar ratio of 50) solutions ranging 50-300 g/L TDS carrying very low quantities of trace elements (created by High Purity Standards, North Charleston, South Carolina) were spiked with 10 $\mu\text{g/L}$ concentrations of a range of REEs, transition metals, precious metals, and high field strength elements to test for element recovery. Matrix recovery was completed in triplicate to provide an honest assessment of variability.

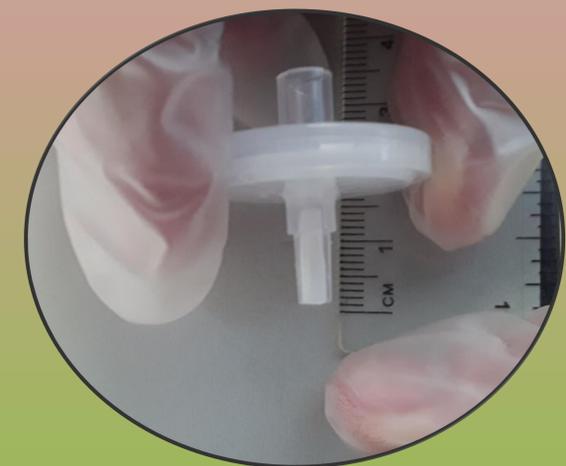


Fig. 2

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Preliminary results:

Impact of Ca and Na: Initial results showed our method was greatly effective removing sodium in both solutions (Na-rich and Ca-rich) even at concentrations of 300 g/L. Sodium recoveries were <0.1% in both solutions (Fig. 7). In the Na-rich solution, Ca was also effectively removed with the highest recovery being just over 0.2%. However, when analyzing the Ca-rich solution, initial findings suggest that the method was not as effective removing Ca, suggesting a challenge in analyzing samples from Ca-rich samples. A re-run of the Ca rich brine will be necessary for further analyses.

Initial element recovery: Our initial results reveal that most REEs, Cu, Ga, Ni, Pb, and Pt recovered well in 50 g/L salinity solutions. These elements were recovered at > 80 % and our labeled Tier 1 in Fig. 8. Tier 2 recoveries range from 40% to 80% and contained many REEs as well as Fe, Mn, Se, Th, U. Tier 3 recoveries were the least successful with values <40%. Most platinum group elements, precious metals, Be, As and B all fell into this tier. Our initial results have revealed that many elements are extremely sensitive to salinity concentrations > 50 g/L. Copper and dysprosium recoveries fared well and have been plotted to show the effects of salinity on their recovery (Figure 9).

Future Research:

pH adjustment: Improvement in recoveries for elements forming oxyanions and high field strength elements has been observed in pH 4 solutions, which will be investigated.

Sample dilution: To increase performance in produced waters at TDS > 50 g/L, effect of diluting sample to a TDS of 50 g/L and running additional sample through the columns (to approximate the same salt load as the original sample) will be investigated.

Standard addition to produced water samples: To examine for performance in actual produced waters, samples from the Permian Basin will be spiked with known masses of CVEs to assess performance of actual produced waters using the proposed methods

Precious metals: Initial results indicate very poor recovery of many precious metals. Alternative ion exchange resins will be investigated, such as Dowex 1-x8.

% RECOVERY OF CU AND DY IN SALINE SOLUTIONS

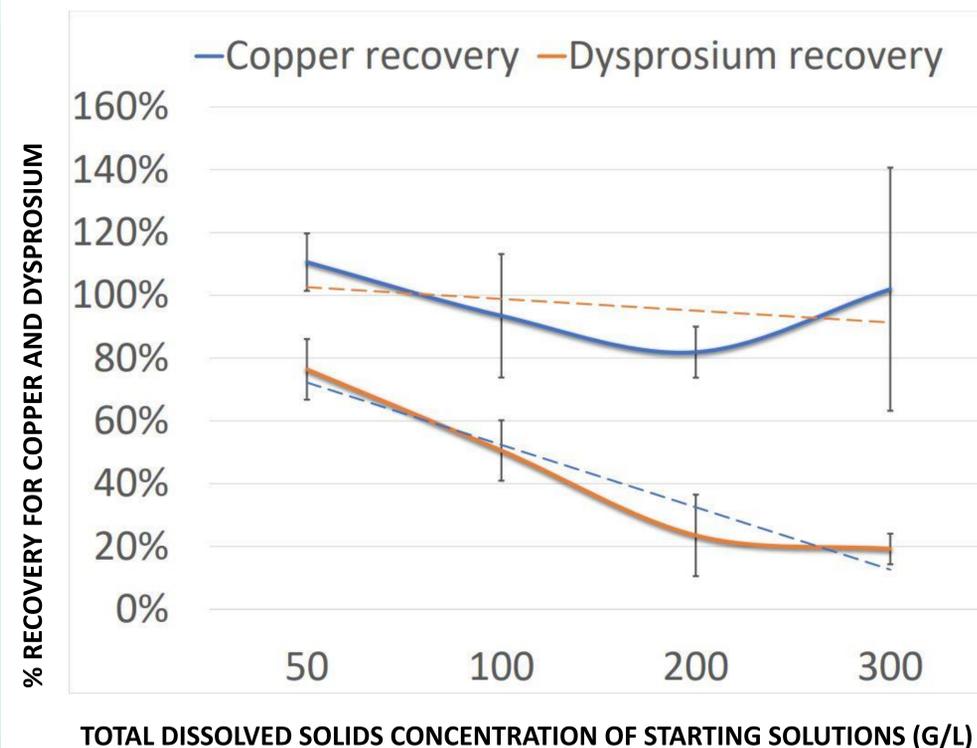


Fig. 9

% RECOVERY OF MATRIX ELEMENTS

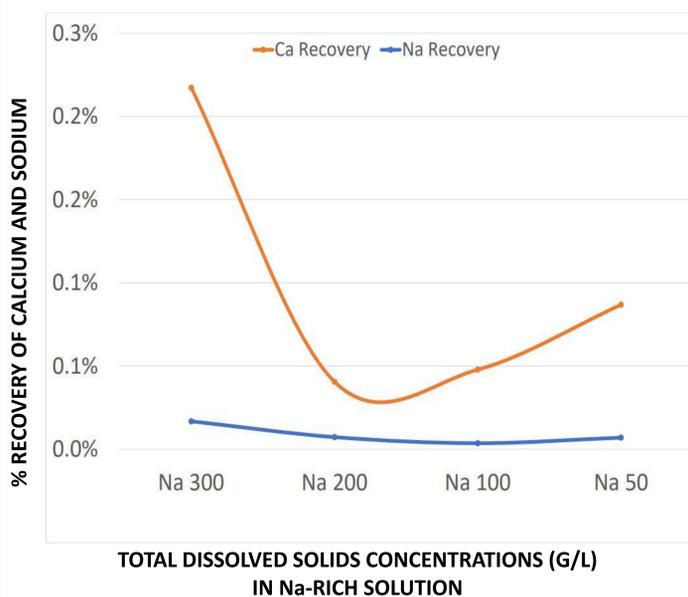


Fig. 7

% RECOVERY OF MATRIX ELEMENTS

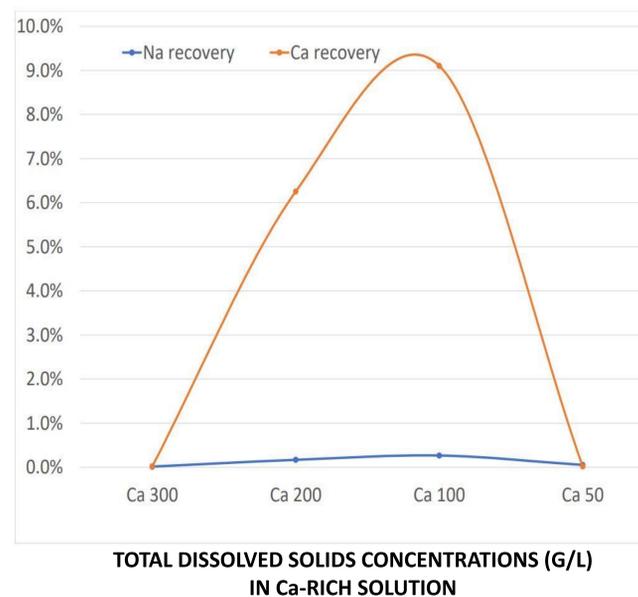


Fig. 8

% RECOVERY OF CVEs

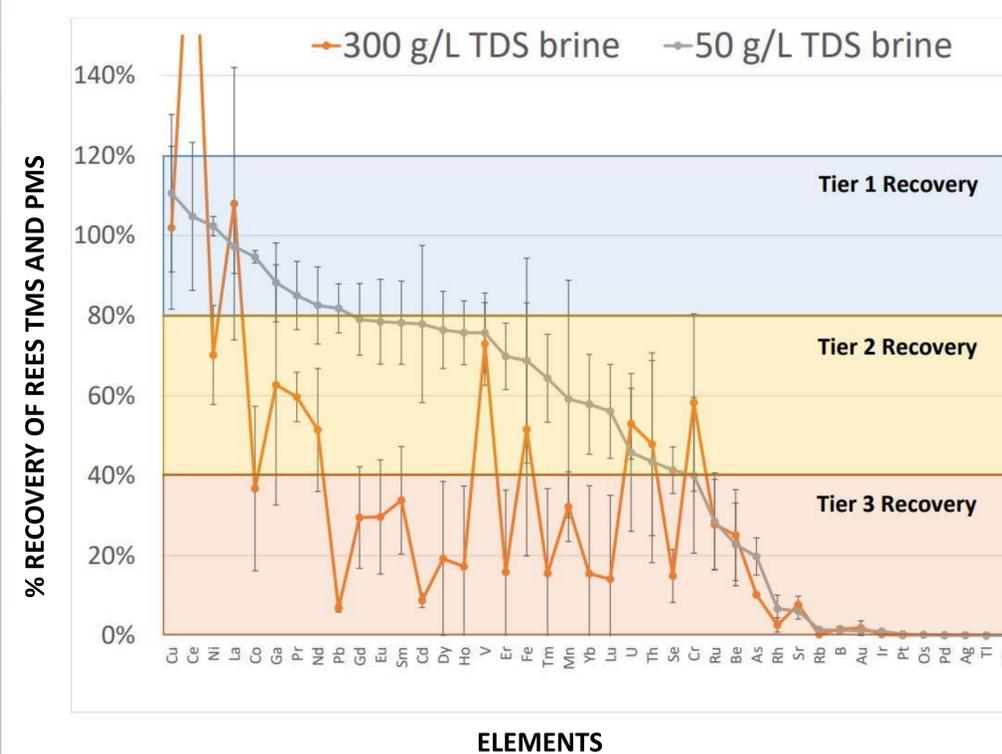


Fig. 8

Acknowledgements:

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References:

Zhu, Y., Itoh, A. & Haraguchi, H. Multielement determination of trace metals in seawater by ICP-MS using a chelating resin-packed minicolumn for preconcentration. Bull. Chem. Soc. Japan 78, (2005) 659-667.