Colorimetric Flow Injection Analysis of Iron(II) in Natural Waters at the Nanomolar Level.

Andrea Higdon, Eric Osantowski, and Michael J. Pullin

Department of Chemistry, New Mexico Tech, Socorro, NM 87801

Abstract

Iron analysis in aqueous solutions is important for water quality control and for understanding redox processes in the environment. Current methods of iron analysis can determine iron(II) and total iron in water samples down to micromolar concentrations. However, in some environments researchers desire to analyze iron at nanomolar concentrations, such as in areas of the ocean where iron is a limiting nutrient. This work details the development and performance of an automated colorimetric analysis method (flow injection analysis) for low iron (II) concentrations in natural waters. This method uses a liquid waveguide flow cell with a 1 meter pathlength to increase the sensitivity of the method. However, increasing the pathlength of the colorimetric analysis method also increases the noise in the analysis, degrading the method's signal to noise ratio and its sensitivity. This work will detail the various sources of noise in this analysis and our efforts to minimize each of them. Overall, this iron(II) analysis method is capable of analyzing iron(II) down to concentrations as low as 1 nM.

Introduction

In this project, we've developed a flow injection analysis (FIA) system for the detection of trace amounts of iron in water samples. FIA is a method that automates wet chemistry and colorimetric analysis methods. FIA systems pump known concentrations of reactants through system of open tubing at a continuous rate. Samples are injected into the system and react to form an observable product. Because flow rates and injection volumes are carefully controlled, FIA systems reduce experimental error, increasing precision and improving detection limits.

Colorimetric analysis with ferrozine has been used for the measurement of iron (II) and total iron (iron(II) + iron(III)). Ferrozine is an organic ligand that forms a purple 3:1 complex with iron(II) (Fig. 1). This ligand is highly specific and doesn't react with iron(III) or with other metal ions in significant amounts. If a chemical reductant is included in the analysis, ferrozine will detect both iron(II) and iron(III), giving a measurement of total iron. As long as the ferrozine is present in excess of the iron, the intensity of the purple colored complex at its absorbance maximum (562 nm) can be used to determine the concentration of iron in the sample

The use of batch-mode methods of analysis limits the use of the ferrozine technique to iron concentrations that are 1 μM and larger. This limit is not low enough for the analysis of many natural waters. The purpose of this study is to lower the detection limit of the ferrozine iron assay by automating the method using FIA techniques.

Methods

In order to increase the precision of the iron-ferrozine method and improve its detection limit, we've automated this technique using FIA (Fig. 2). The iron(II)-ferrozine complex formed during the analysis is measured using a flow-through absorbance detector. The detector is a fiber optic liquid capillary waveguide that has a 1 m pathlength. The relatively long path of the waveguide detector should increase the detection limit of the method 100-fold over the use of the standard 1 cm path HPLC detector. However, the increased sensitivity also increased the baseline noise of the FIA system. Thus, we needed to be careful of each component in the system that could contribute to pressure or flow rate fluctuations in the system, as these fluctuations would lead to increased baseline noise. For example, we had to

abandon the use of a syringe pump in the FIA system as each step of the syringe drive motor would cause an observable baseline fluctuation.

Additionally, the increased sensitivity made an interference from the differing index of refraction between the carrier fluid and the samples problematic. The index of refraction is caused by a change in salinity between the carrier stream and the sample. This produced large negative absorbance peaks. The negative peaks were a problem at the low concentration end because they drowned out the positive signal from iron absorbance. This problem was solved by making our standard solutions in the carrier fluid and also spiking samples with the carrier components.

For the analysis of iron(II), a 10 mM MES buffer was pumped into the system using an HPLC pump at 1.0 mL/min. Iron samples are introduced into the MES buffer using a 6-way HPLC injection valve and a 250 ml sample loop. A 10 mM Ferrozine solution was pumped into the system using a syringe pump at a rate of 0.1 ml/min. The MES buffer and ferrozine solution are mixed together using a mixing T, followed by a length of knotted tubing that forms a a reaction chamber. The mixed solution then enters the liquid waveguide capillary cell. Data was continuously collected from the liquid waveguide capillary cell using Labview.

Results and Discussion

Figure 1: The chemical structure of Ferrozine.

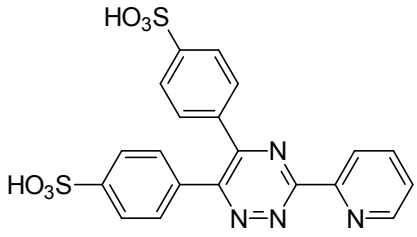


Figure 2: System layout

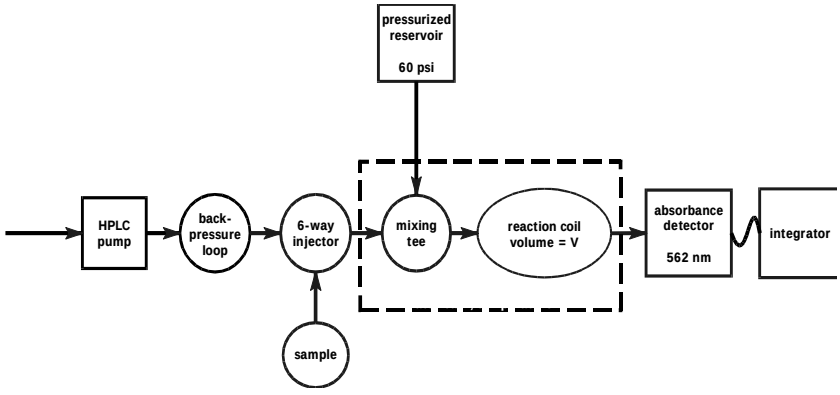


Figure 3: Example of iron FIA data. Each peak is a injection of an iron(II) containing solution.

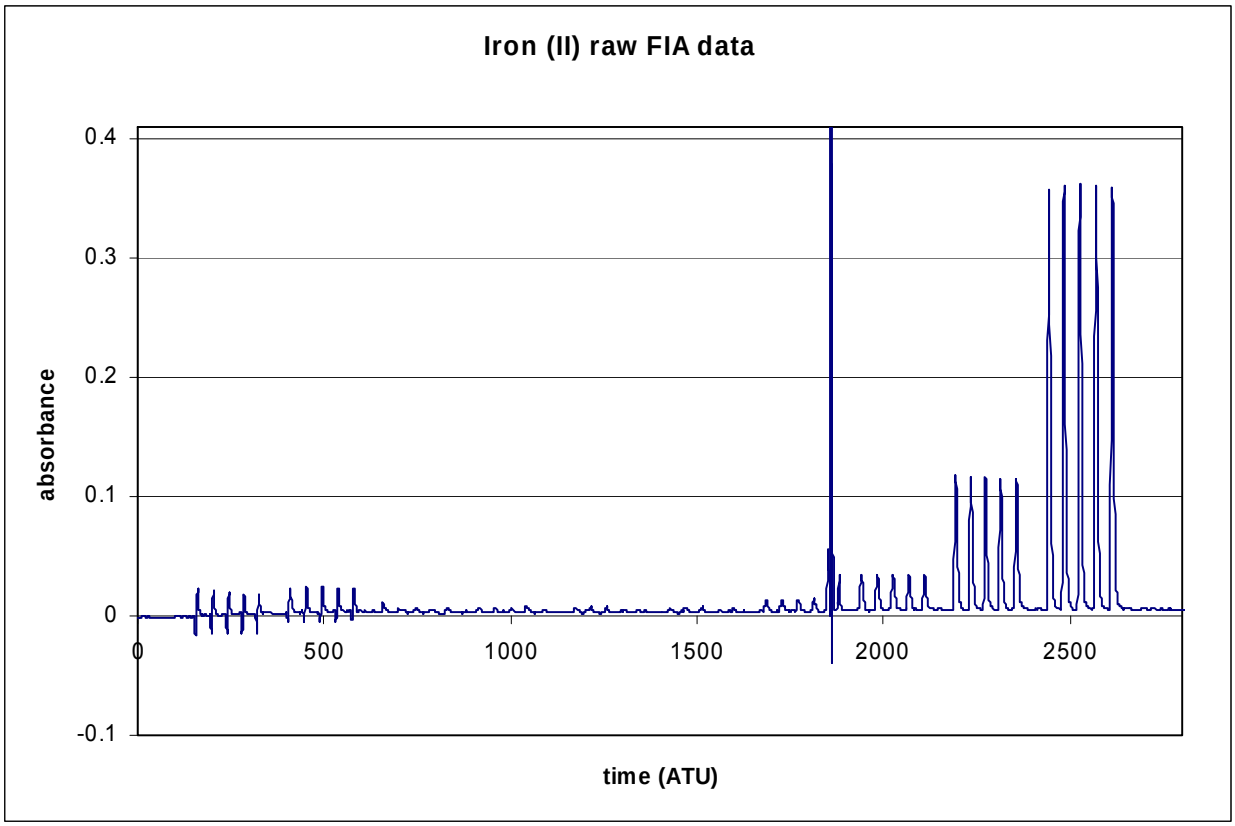
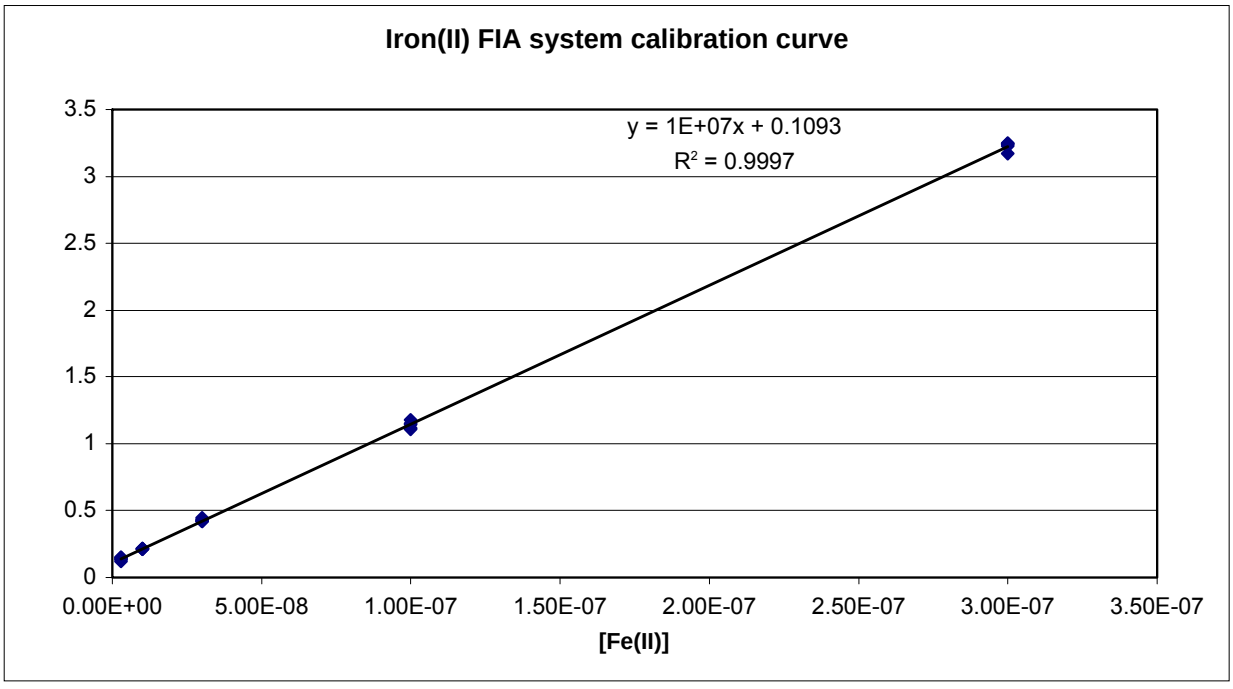


Figure 4: Calibration curve using the FIA method.



The linear range for the liquid waveguide capillary cell was 1.0×10^{-9} to 1.0×10^{-6} M iron. The detection limit for the liquid waveguide capillary cell is what we expected based on its pathlength and the molar absorptivity of the iron(II)-Ferrozine complex.

We are currently preparing a journal article for submission to *Environmental Science and Technology* that describes this research. Submission is expected by the end of this calendar year.

Future research

Due to delays in developing the FIA system caused by the noise issues described above, we did not have a chance to apply this system to analysis of water samples from Valles Caldera, as we had proposed. Additionally, for the same reasons, the work has only been presented at the WRRI conference this past summer. However, future research is planned that will include studying the kinetics of iron(II) oxidation in natural systems. We are also interested in the effect microbes play in the oxidation of iron in natural water systems. The recently funded New Mexico EPSCoR grant will provide us with funding to develop and deploy an in-stream iron(II) sensor based on this technology.