Determination of iron in nanomolar concentrations in natural waters

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Chemistry of iron

- Iron is an element of great environmental significant with two commonly observed oxidation states in natural waters, Fe(II) and Fe(III).
- Fe(III) is thermodynamically stable in oxygenated systems; however, quickly hydrolyzes and precipitates at circumneutral pH values and becomes biologically unavailable.
- Fe(II) is more soluble and involves in a number of iron uptake strategies by microorganisms.
- Fe(II) oxidizes rapidly in oxygenated waters with a half- life on the order of minutes at around pH 8.
- Dissolved organic matter also complexes with iron and involves in variety of photochemical and non photochemical reactions.
- Photochemical reduction of Fe(III)-DOM complexes are a major source of bioavailable Fe(II) in sunlit waters and also helps to regulate DOM.

Determination of Fe

- The accurate determination of Fe(III) and Fe(II) in natural waters at very low concentrations is essential to understand the biogeochemistry of iron in these environments.
- Conventional analytical methods for the determination of Fe such as ICP-OES, ICP-MS, AAS do not provide any information about its oxidation state and also not applicable in the field.
- Chemiluminescence methods are very sensitive; however, suffers from interferences from DOM.
- Colorimetric methods use iron sensitive ligands such as ferrozine to make colored complexes. The intensity of the color is proportional to the concentration of iron when the ligand is present in excess of iron
- Colorimetric methods are not sensitive to higher DOM concentrations or the temperature variations during the analysis. However, they have worst detection limits with bench-top spectrophotometers equipped with optical cells of 1 to 10 cm.
- Sample preconcentration techniques and longer optical cells (few meters) have been used successfully to improve the detection limit.

Flow injection analysis: FIA

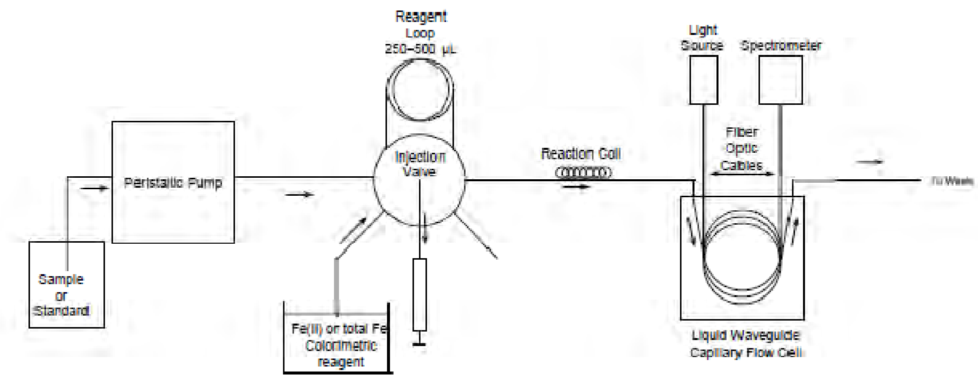
- It is a type of continuous flow analysis that utilizes an analytical unsegmented stream, into which highly reproducible volumes of samples are injected.
- The analytical stream can be either a flowing reagent stream or a inert carrier stream.
- FIA operates under laminar flow conditions. The sample induced dispersion is used for controlled sample mixing with the analytical stream.
- All the samples must have similar residence times and must expose to identical the environmental conditions in the analytical stream for reliable and reproducible data.
- The maximum detector response is achieved when an optimum balance is reached between the sample dispersion and the reaction time.
- Radical diffusion (secondary flow) also acts as a efficient scrubbing mechanism and sample carryover and sample cross contamination.

Reverse FIA

- Reverse flow injection analysis (rFIA) injects small volume plugs of reagents into a flowing sample or a calibration standard stream.
- Operational conditions and principles are similar normal FIA
- Minimize the reagent consumption when the sample availability is not a concern.
- Ideal for *in situ* analysis.
- Both FIA and rFIA are highly versatile and easy to automate.

rFIA Instrumentation

Pump	MasterFlex® L/S Peristaltic pump
Tubing	0.03” ID FEP
Data acquisition	LabVIEW®
Injection valve	Rheodyne® 6 way manual
Light Source	Ocean Optics LS-1
Detector	Ocean Optics USB 2000 mini spectrophotometer
Reaction coil	24”, 48” or 60” long knotted 0.03” ID FEP tubing
Injection Loop	250µL, 350 µL, 400µL or 500µL made out of 0.03” ID FEP tubing
Cell	World Precision liquid waveguide capillary cell 1.0 m



Reagents & Calibration Standards

- All the reagents and standards are prepared in thoroughly rinsed polypropylene plastic ware.

- Fe(II) standard solution (0.01M)

  Prepare on weekly basis using $Fe(NH_4)_2(SO_4)_2$ (S) in 0.01 M trace metal grade HCl.

- Total Fe standard solution (0.018M)

  Uses a iron AAS single element standard solution 0.018 M.

- Fe(II) calibration standards (1.0 x 10-6 M to 1.0 x 10-9 M)

  Prepare on daily basis using the 1.0 x 10-4 M working standard solution.

- Total Fe calibration standards (1.8 x 10-6 M to 1.8 x 10-9 M)

  Prepare on daily basis using the 1.8 x 10-4 M working standard solution.

Reagents & Calibration Standards Cont…

- Fe(II) colorimetric reagent

  Appropriate amount of ferrozine is dissolved in a 0.1M MES buffer adjusted to pH 6.

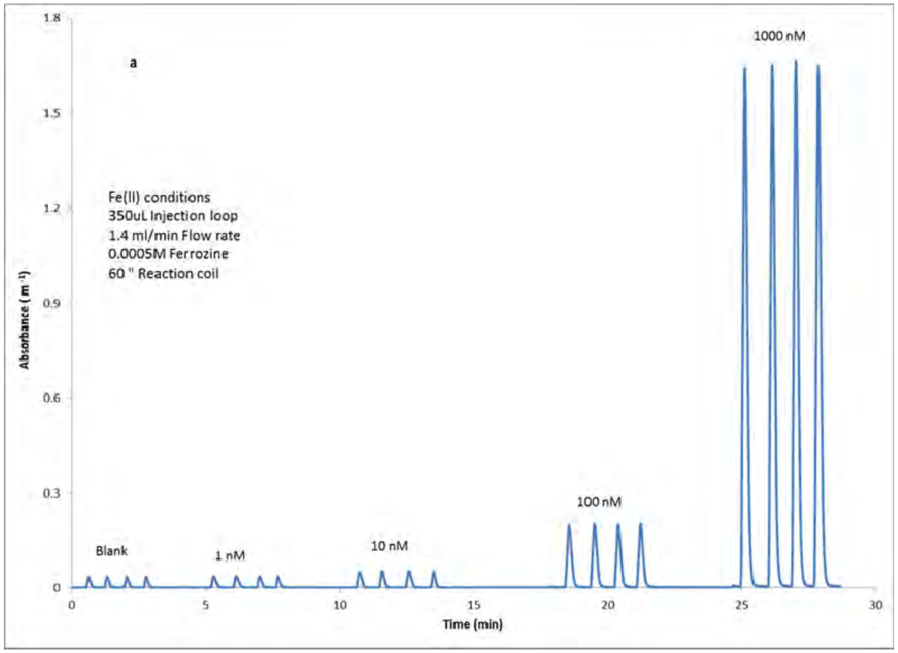
- Total Fe colorimetric reagent

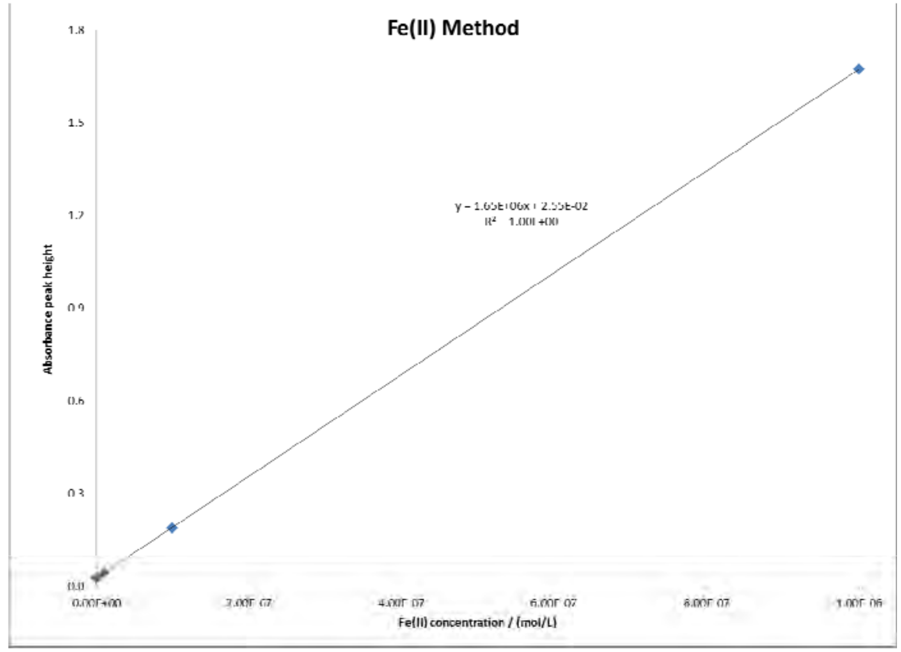
  Appropriate amount of ferrozine is dissolved in 0.1M acetate buffer adjusted to pH 4.

  The acetate buffer contains 0.10 M trace metal grade acetic acid, 0.10 M ascorbic acid and 1 mM citric acid.

- Semiconductor grade concentrated NaOH is used for pH adjustments

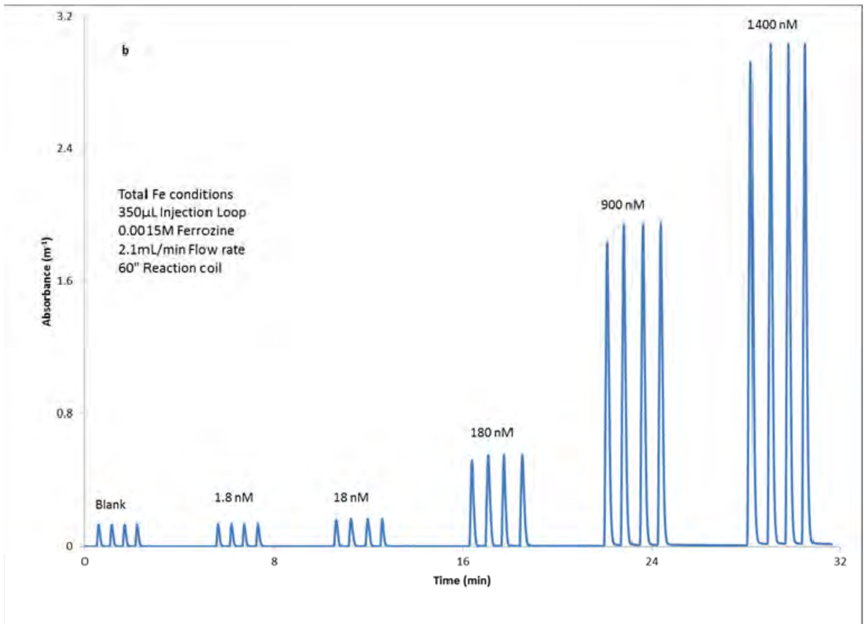
Detector response – Fe(II) Method

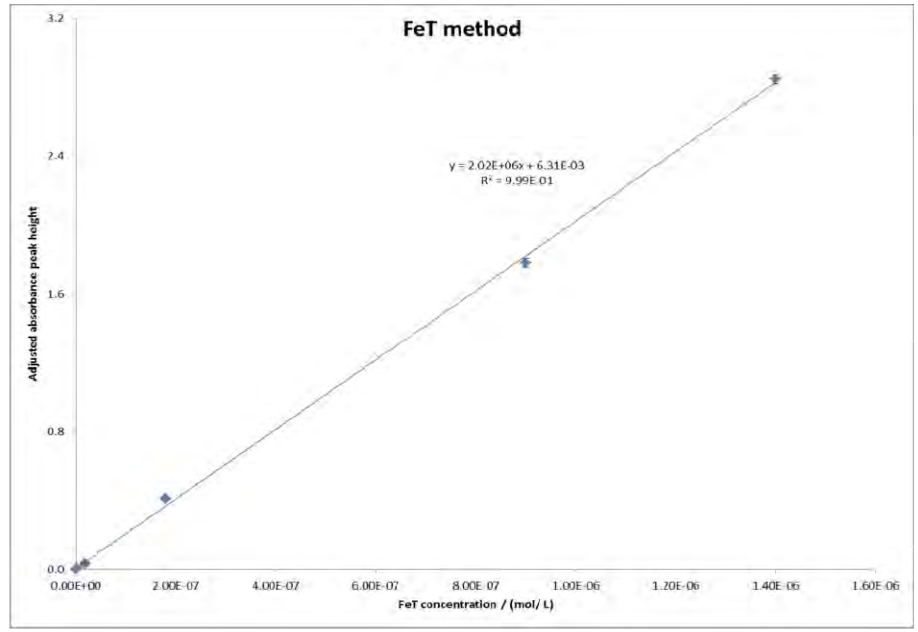




Reaction coil	60”
Flow Rate	1.4 mL/min
Colorimetric reagent	0.1 M MES buffer adjusted to pH 6 & 0.0005M Fz
Injection loop volume	350µL

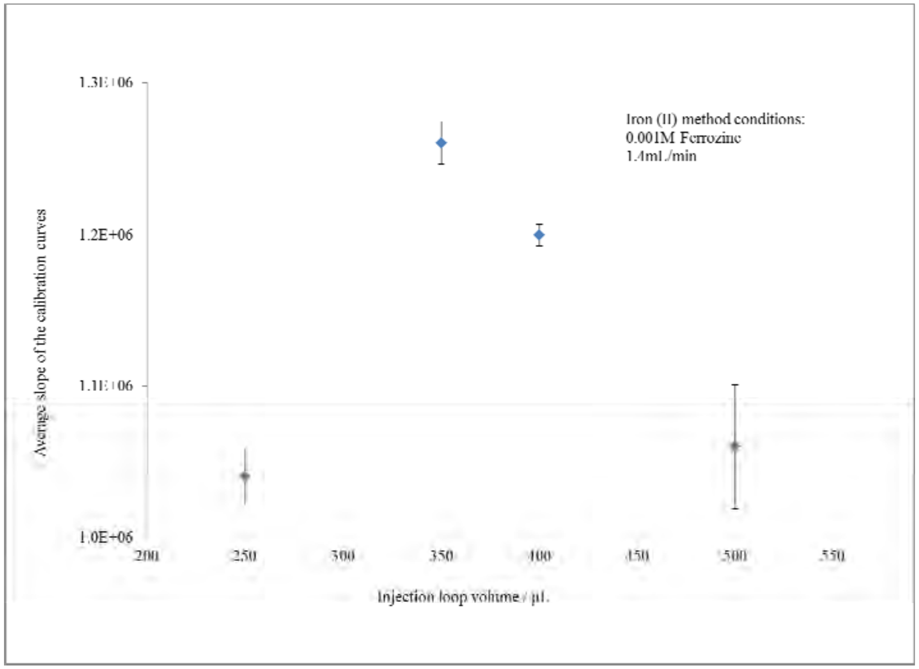
Detector response - FeT Method

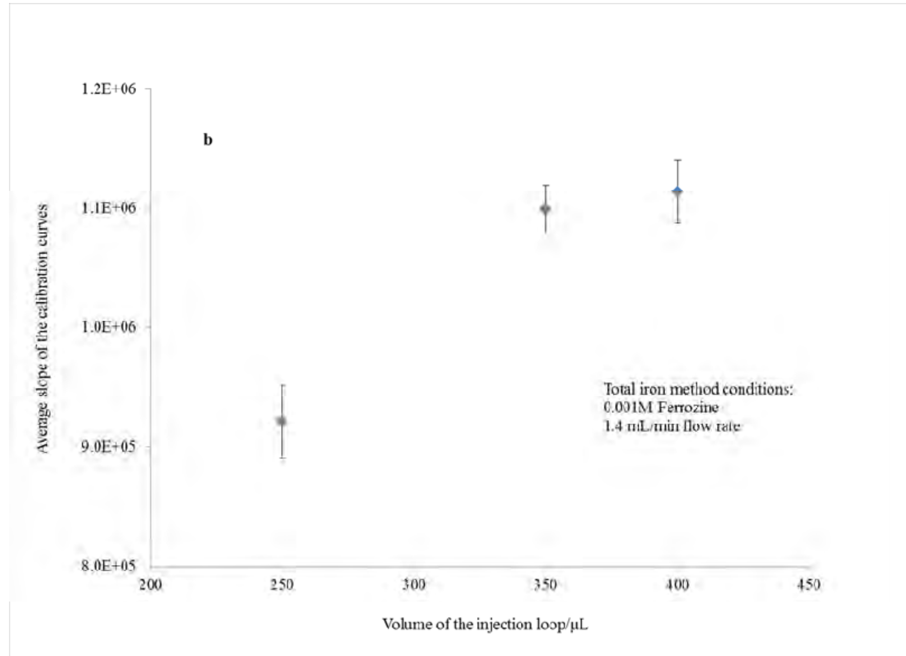




Reaction coil	60”
Flow Rate	2.1 mL/min
Colorimetric Reagent	0.1M Acetate buffer pH 4 , 0.1M Ascorbic acid 0.001M Citric acid & 0.0015 Ferrozine
Injection loop volume	350µL

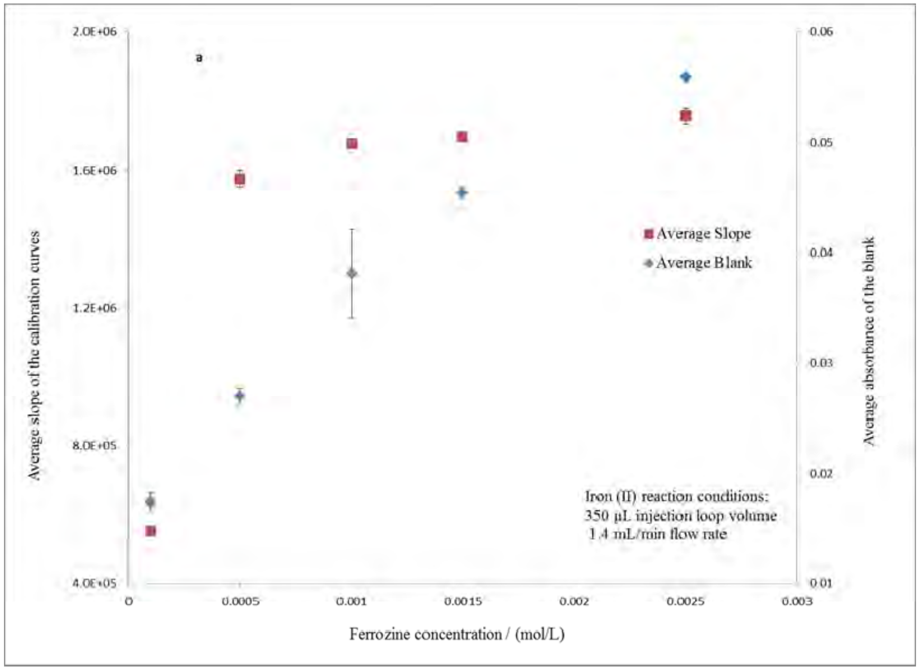
Volume of the Injection loop

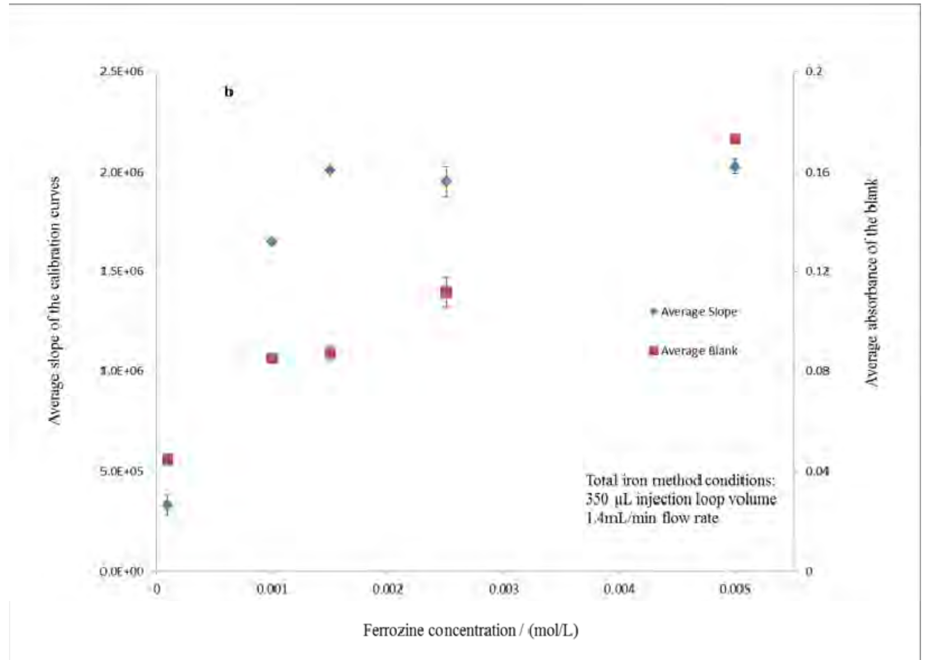




	Fe(II) Method	FeT Method
Reaction coil	60”	60”
Flow Rate	1.4 mL/min	1.4mL/min
Colorimetric reagent	0.1 M MES buffer pH 6 0.001M Fz	0.1M Acetate buffer pH 4, 0.001M Fz 0.1M Ascorbic acid
Optimum injection loop volume	350µL	350µL

Ferrozine concentration





	Fe(II) method	FeT Method
Reaction coil	60”	60”
Flow Rate	1.4 mL/min	1.4mL/min
Colorimetric reagent	0.1 M MES buffer pH 6 Ferrozine	0.1M Acetate buffer pH 4 , 0.1M Ascorbic 0.001M Citric acid & Ferrozine
Injection loop volume	350µL	350µL
Optimum ferrozine concentration	0.0005 M	0.0015M

Flow rate

Fe(II) Method

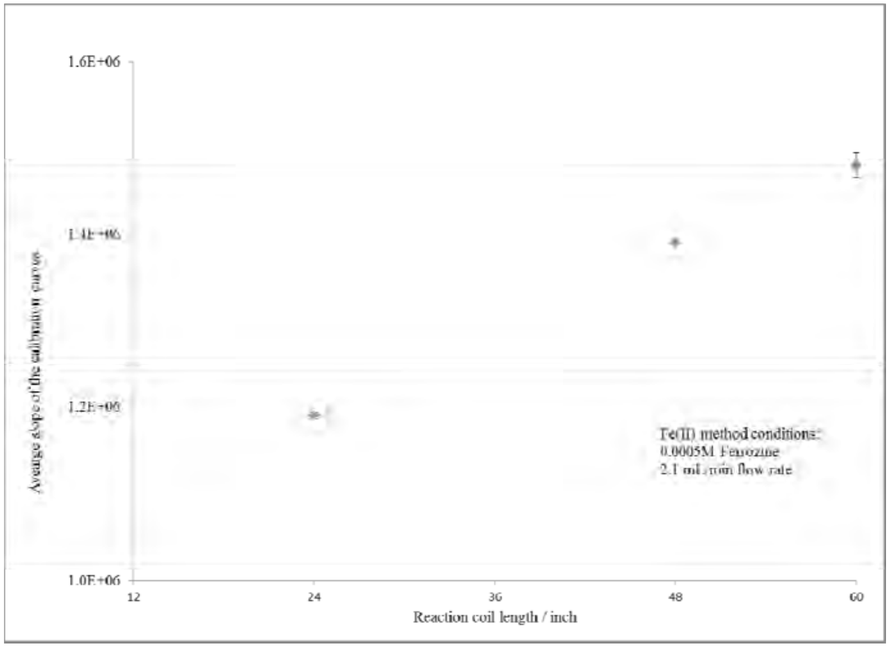
Flow rate (mL/min)	Average slope of the calibration curves
1.4	1.55×10^6
2.1	1.55×10^6

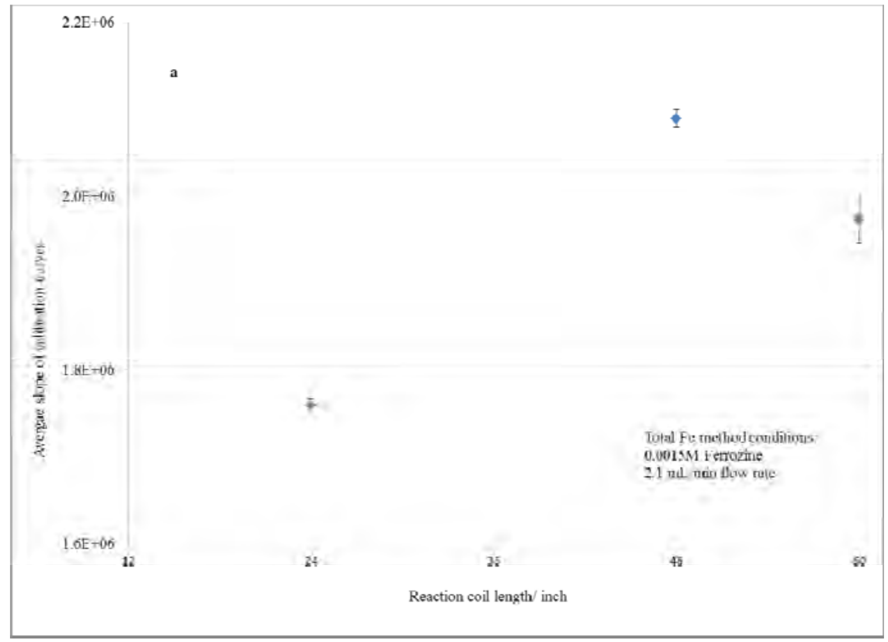
Total Fe method

Flow rate (mL/min)	Average slope of the calibration curves
1.4	1.91×10^6
2.1	1.94×10^6

	Fe(II) method	FeT Method
Colorimetric reagent	0.1 M MES buffer pH 6 0.0005M Ferrozine	0.1M Acetate buffer pH 4 , 0.1M Ascorbic 0.001M Citric acid & 0.0015M Ferrozine
Injection loop volume	350µL	350µL
Reaction coil length	60”	60”
Optimum flow rate	2.1 ml/min	2.1mL/min

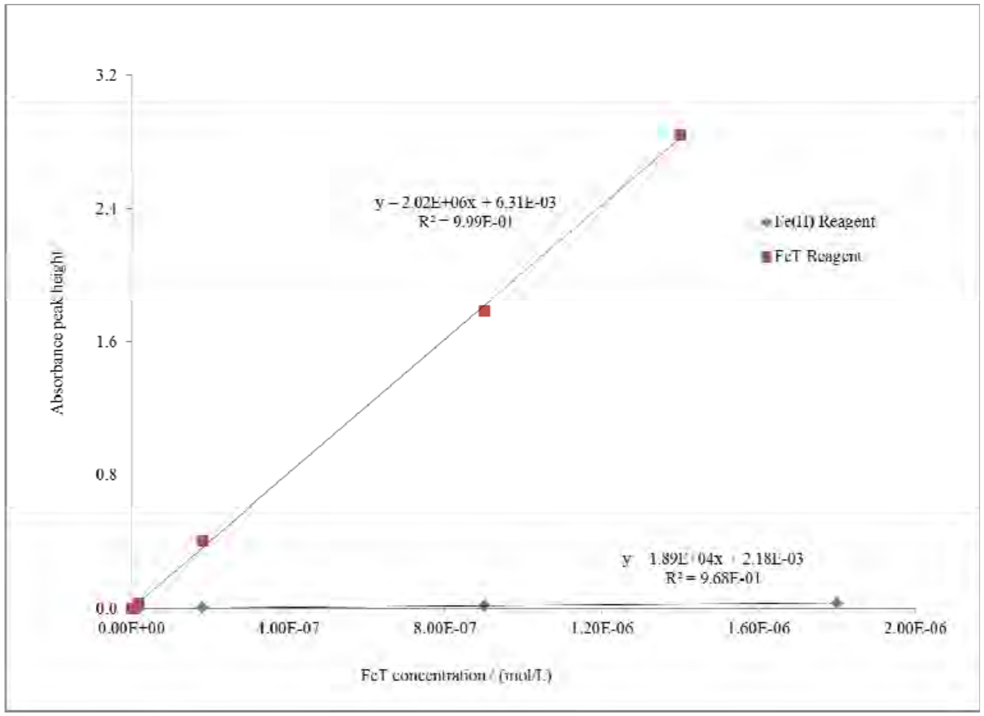
Reaction coil length





	Fe(II) method	FeT Method
Flow Rate	2.1 mL/min	2.1 mL/min
Reaction solution	0.1 M MES buffer pH 6 0.0005M Ferrozine	0.1M Acetate buffer pH 4 , 0.1M Ascorbic 0.001M Citric acid & 0.0015M Ferrozine
Injection loop volume	350μL	350μL
Optimum reaction coil length	60”	60”

Selectivity between Fe(II) method and total Fe method



Total iron determination

Using the total iron colorimetric reagent

Using the iron(II) colorimetric reagent

Analytical characteristics of the system

	Fe(II) system	Total Fe system
Injection volume	350μL	350μL
Ferrozine concentration	0.0005 mol/L	0.0015 mol/L
Flow rate	2.1 mL/min	2.1 mL/min
Reaction temperature	Room temperature	Room temperature
Detection Limit	$1.2 \pm 0.2 \times 10^{-9}$ mol/L	$7.2 \pm 1.5 \times 10^{-10}$ mol/L

Determination of the total Fe concentrations in natural waters

Sample	Total Fe concentration (rFIA)x 10^{-8} (mol/L)
Upper Jaramillio	10.6 ±0.2
Upper Upper Jaramillio	6.1 ±0.1
East Fork Bridge	7.1 ±0.2
La Jara	6.0± 0.1
Rio Grande	2.0± 0.02
Surface water site S1 of East Fork	6.70± 0.06

Applications

- The method will be used to develop an automated *in-situ* iron analyzer