

A multi-syringe flow injection system using a long liquid waveguide capillary flow cell and a chelating resin for the ultra trace determination of iron in waters



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Introduction

Iron plays an important role in phytoplankton productivity and therefore affects the temperature cycle through the fixation of carbon dioxide by the phytoplankton. In natural waters it's present at very low concentrations. To overcome the detection difficulties arising from the low levels of iron in waters, a liquid waveguide capillary cell (LWCC) and a preconcentration column (NTA superflow resin and Chelex 100) were used. The spectrophotometric determination was based on the colorimetric reaction between iron (III) and ammonium thiocyanate or iron (II) and ferrozine. For flow manipulation/programming a multi-syringe flow injection analysis (MSFIA) was developed.

Manifold

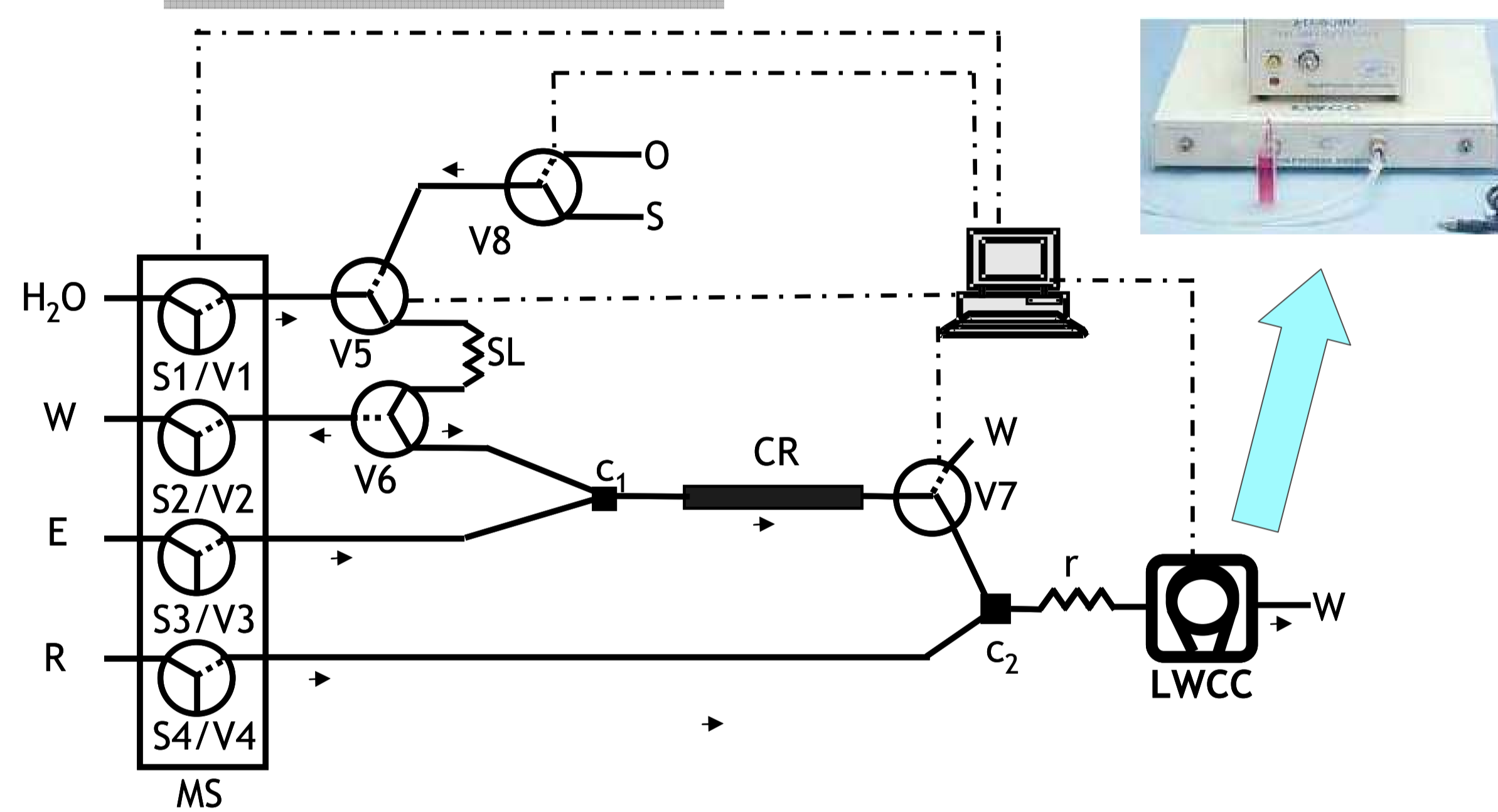


Figure 1. Multi-syringe flow injection analysis manifold for the determination of iron in waters. S: syringes, V: solenoid valves in position "on" (discontinuous line) or "off" (continuous line); SL: sample loop (2 mL); r: reaction coil; c: confluence; LWCC: detector (100 cm of optical path, 480 and 562 nm for ammonium thiocyanate and ferrozine, respectively); MS: multi-syringe module; CR: chelating resin (NTA or Chelex 100); W: waste; S: sample or standard; O: oxidant (and conditioning agent for Chelex 100 resin); E: eluent; R: color reagent (ammonium thiocyanate or ferrozine)

Protocol sequence

| Step | Piston movement | Position of syringes and solenoid valves | | | | | | | | Volume (mL) | Flow rate (mL/min) | Description | |
|------|-----------------|--|-----|-----|-----|-----|-----|-----|-----|-------------------|--------------------|-------------|--|
| | | S 1 | S 2 | S 3 | S 4 | V 1 | V 2 | V 3 | V 4 | | | | V 5 |
| 1 | Dispense | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 2.6 | 4 | Cleaning the chelating resin |
| 2 | Pick up | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 0/1 | 1.4 s. / 1.1 c.a. | 1.4 | 5 | Aspirate sample and oxidant |
| 3 | Dispense | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 2.5 | 2.5 | Propel sample through the resin |
| 4 | Dispense | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0.5 | 2.0 | Propel eluent through the resin |
| 5 | Dispense | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0.5 | 2.0 | Propel eluent and reagent to the detector |
| 6 | Dispense | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.9 | 2.5 | Propel the mixture to the detector and signal registration |

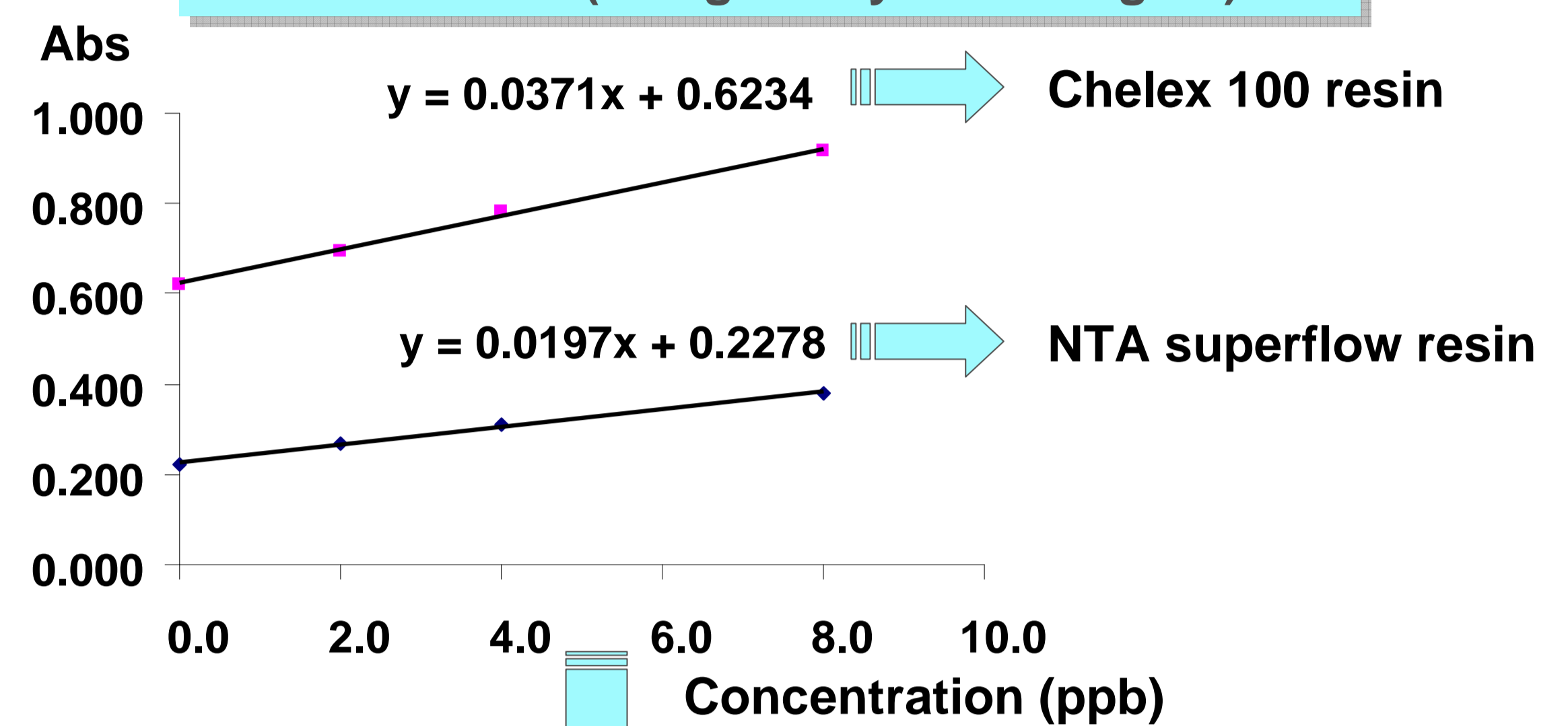
Note: 0- off; 1- on; The volume and the flow rate are presented with respect to syringe 1. Syringe 1 and 2 have 5 mL of capacity and syringe 3 and 4 have 2,5 mL of capacity; s.- sample or standard; c.a.- conditioning agent;

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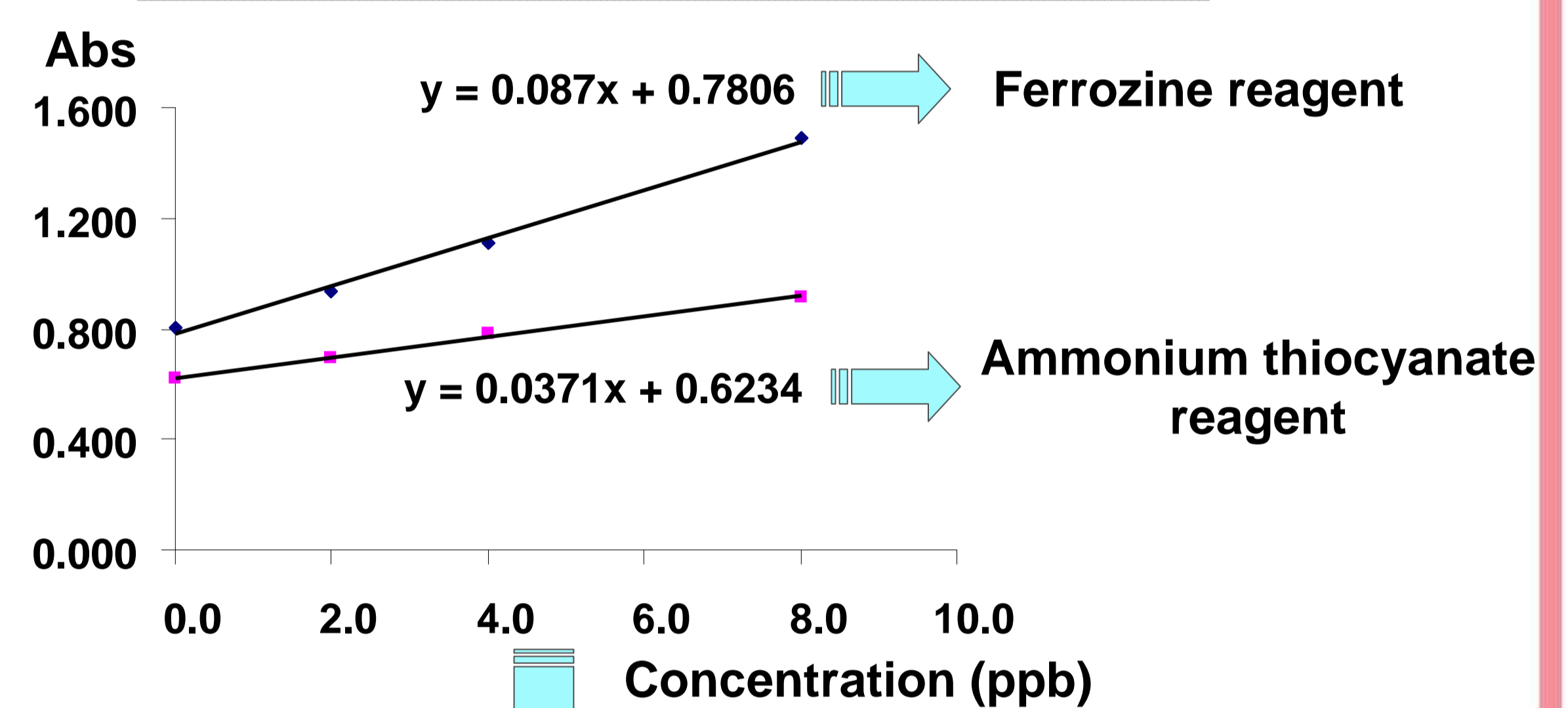


Comparison of the preconcentration columns (using thiocyanate reagent)



The Chelex 100 resin has a higher capacity to concentrate iron (III) than NTA superflow resin

Comparison of the reagents using the chelex 100 resin



The ferrozine reagent has a higher sensitivity than ammonium thiocyanate reagent

Figures of merit

| Resin | NTA superflow | Chelex 100 | Chelex 100 |
|----------------------------------|---------------|-------------|------------|
| | Thiocyanate | Thiocyanate | Ferrozine |
| Detection limit (ppb) * | 0.52 | 0.56 | |
| Quantification limit (ppb) | 1.16 | 1.15 | |
| Working range (ppb) | 0-50 | 0-20 | 0-15 |
| Determination rate /h | 15 | 15 | 15 |
| Reagent consumption (mmol/assay) | | | |
| HCl | 0.25 | 0.25 | 0.25 |
| Thiocyanate ammonium | 0.38 | 0.38 | --- |
| Ferrozine | --- | --- | 0.00062 |
| Acetic acid | --- | 0.28 | 0.28 |
| Sodium acetate | --- | 0.80 | 0.80 |
| Ascorbic acid | --- | --- | 0.028 |

* - assessed from three times the standard deviation from blank signal (n=10)

Legend: --- not applied

There was no improvement in the detection limit due to higher blank signal

The combination of NTA superflow with ferrozine reagent will be tested