



A multi-syringe flow injection system for the spectrophotometric determination of trace levels of iron in waters using a liquid waveguide capillary cell and different chelating resins and reaction chemistries

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ABSTRACT

A method integrating a long waveguide capillary cell with a preconcentration resin in a multi-syringe flow injection analysis (MSFIA) system for iron determination in waters was developed. The determination of iron is based on a colorimetric reaction and two reagents were tested, ferrozine and ammonium thiocyanate. A liquid waveguide capillary cell (1.0 m pathlength, 550 μm i.d. and 250 μL internal volume) with a preconcentration resin were used to improve the sensitivity of the determination. Two different preconcentration resins were also tested, Chelex 100 and NTA Superflow. The developed method employing the NTA Superflow with ferrozine colorimetric reagent provided a detection limit of 0.05 $\mu\text{g L}^{-1}$ with a linear response up to 8 $\mu\text{g L}^{-1}$ and a sample throughput rate of 12 per hour. The developed system presents low reagents/sample consumptions. The accuracy was assessed using a certified reference water sample.

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1. Introduction

Iron is one of the most frequently determined analyte in environmental (like water, soil and sediment) samples [1]. This fact can be naturally attributed to the significant role of this analyte in the environmental geochemical cycles. In the last decades, the knowledge of the concentration of iron in natural waters is gaining importance. Despite being one of the most abundant elements on earth crust, it occurs at very low levels in ocean waters (3–112 ng L^{-1}) being a limiting nutrient for phytoplankton growth [2,3]. As it is recognized now, variation of iron concentration can ultimately affect the oceans carbon cycle and has consequent implications in climate change [4].

The main form of iron in waters is iron (III), however only a small fraction occurs in a free hydrated form. Iron (II) is highly soluble but rapidly oxidized to iron (III) [5]. It is present at very low concentrations levels in waters and its determination is particularly difficult because of the complexity of the matrix and also because of the different physical, chemical and biological processes involved [6]. Furthermore, iron is omnipresent in many materials and equipment, increasing the risk of contamination [5]. In order to overcome these difficulties and to increase sensitivity, separation and/or preconcentration is an important and frequently applied tool [7].

There is a wide variety of possible instrumental methods, spectrophotometry [8–10], chemiluminescence [11], HPLC [12], adsorptive

stripping voltammetry [13], fluorescence [14], inductively coupled mass spectrometry (ICP-MS) [15] and atomic absorption spectrometry (AAS) [16] for detection of iron. However when trace levels of the analyte is concerned, the applicable detection methods are reduced.

Flow analysis systems provide several advantages for sample manipulation including simplicity, equipment cost, accuracy, good reproducibility, elevated sample throughput, in-line sample manipulation, high degree of automation and reduction in the consumption of samples/reagents and in effluent production [8,17,18].

There are several spectrophotometric systems for iron determination using different flow strategies. Some of these applications use this determination as a case study to demonstrate the capabilities of some newly developed flow handling techniques. In this context, Pons et al. summarizes the development and improvement of flow procedures based on using the same reaction chemistry for the determination of iron in different flow strategies [19]. Within the published spectrophotometric flow methods there are several that use preconcentration/separation approaches incorporated in FIA [20], SIA [21], MSFIA [10] and multi-pumping [9] manifolds.

MSFIA is one of the most recent flow analysis techniques and it was first proposed by Cerdà and co-workers [22]. Among with other flow analysis techniques, it offers high sampling rate, robustness, versatility and low consumption of reagents and samples [23]. MSFIA combines the multi-channel operation of flow injection analysis with the ability to select the exact volumes of sample and reagents needed for analysis, as it is carried out in sequential injection analysis (programmable flow) mode. One not frequently mentioned, but not less important characteristics of the MSFIA system is that it is also able to work under

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moderate backpressure, thus is very suitable when using intercalated resins [18,19] or even monolithic columns [24].

Various resins are described in literature as C18 [20], Amberlite XAD-4 [25], MAF-8HQ [26], 8HQ [27], Chelex 100 [19,21] and NTA Superflow [7,28] for iron preconcentration. The latter NTA Superflow resin was originally designed for high throughput sample clean-up procedures based on the affinity chromatography concept. It presents several advantages as, the analyte recovery at low pH and the supported high flow rates which is very interesting for using in applications where high sampling rate is needed. Recently, this commercial resin was applied for the preconcentration of total iron in low pH open sea water samples [7]. The developed work presented remarkable analytical characteristics; those in one part can be attributed to the new resin and in other part to the applied ICP-MS detector.

One objective of this work was to apply and compare the characteristics of the NTA resin to the well established Chelex 100 cationic exchange resin (operating at a higher ≈ 4 pH range), under flow analysis conditions and using a spectrophotometric detection system with a liquid waveguide capillary cell. In the LWCC, the spectrophotometric pathlength is increased without considerable light attenuation [29]. The light is carried by means of an optical fiber to the LWCC where it undergoes total internal reflection on the cell walls. The potential to exploit this equipment was only possible since 1993 with Teflon AF-2400 (DuPont Fluoroproducts, DE, USA). This polymer is chemically stable, inert and is mainly transparent through UV and visible range with refractive index (1.29) lower than water (1.33) [30].

The ultimate objective of the work was to develop an automated method capable to detect and quantify low levels of iron in waters, with minimized reagent consumption. For this purpose the LWCC and a preconcentration mini-column were coupled to a MSFIA system. Two different chemistries were applied for downstream spectrophotometric detection of iron in the different oxidation states of Fe^{2+} and Fe^{3+} , involving the colorimetric reagents ferrozine and ammonium thiocyanate, respectively.

2. Experimental

2.1. Reagents and solutions

Ultra pure water from a MilliQ system (resistivity $> 18 \text{ M}\Omega \text{ cm}^{-1}$) was used for the preparation of all solutions and all chemicals were analytical-reagent grade. Iron (III) stock standard solutions (10 mg L^{-1}) were prepared by diluting commercial 1000 mg L^{-1} iron atomic absorption standards (VWR-Spectrosol) in 0.01 mol L^{-1} HCl solution. Within the linear response range, several working standard solutions from 1 to $8 \mu\text{g L}^{-1}$ in 0.01 mol L^{-1} HCl solution were prepared daily from the stock solution. Iron (II) stock standard solution (100 mg L^{-1}) was prepared by dissolving ammonium iron (II) sulphate hexahydrate (Merck) in 0.01 mol L^{-1} HCl solution. River water certified reference material (NCR-SLRS-4) was also analysed for the evaluation of the accuracy of the developed method as recommended by the National Council of Canada.

Ferrozine solution of 2.5 mmol L^{-1} was prepared daily by dissolving 0.0185 g of ferrozine reagent ($\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_6\text{S}_2$) in a 2% (w/v) ascorbic acid solution prepared in a 2 mol L^{-1} acetic acid ammonium acetate solution where the final pH was adjusted with acetic acid to 4.5.

The ammonium thiocyanate solution of 1.5 mol L^{-1} was prepared by dissolving 11.4 g of the solid ($\text{CH}_4\text{N}_2\text{S}$) in a 100 mL of MilliQ water.

The Chelex 100 resin (Bio-Rad, 200–400 mesh, sodium form) was suspended in a conditioning buffer obtained from 6.56 g of sodium acetate and 16 mL of concentrated acetic acid solution in 200 mL of water and with final pH adjusted with acetic acid to 4. The same procedure was adopted to prepare the conditioning buffer/complexing agent solution, with water being replaced by a 1 mol L^{-1} sodium chloride solution. The 1 mol L^{-1} sodium chloride solution was prepared by dissolving 5.84 g of sodium chloride in 100 mL of water.

The resin NTA Superflow resin (Qiagen Inc., Valencia, CA) is available in a form of suspension therefore it is ready to use.

The resins were packed in PVC tubing (2.22 mm i.d. and 2.5 cm length) and the suspensions introduced into the column by means of Pasteur pipette. Ordinary dishwashing foam was placed at both ends of the column to entrap the resins inside. Before application to iron determination the prepared resin columns were washed with 1.0 mol L^{-1} HCl solution, until stable ($\text{RSD} < 3\%$) blank reading was obtained.

2.2. Apparatus

Solutions were propelled through a multi-syringe burette (Crison Instruments, Allela, Spain). The device uses a multiple-channel piston pump, containing up to four syringes, driven by a single motor, controlled by computer software through a serial port. Three-way commutation valves (NResearch, Caldwell, NJ, USA) were connected at the head of each syringe.

Two syringes of 10 mL were placed in position 1 and 2 and two syringes of 2.5 mL were placed in positions 3 and 4. Hamilton (ref. 81620 and 81420) glass syringes were used. The piston movement of the multi-syringe was divided in 16,000 steps, therefore the minimum volume delivered was 0.62 for the 10 mL syringes and $0.16 \mu\text{L}$ for the 2.5 mL syringes. For all solenoid valves, the exchange options were classified in on/off lines. The “on” line was assigned to the flow network and the “off” line to the solution flasks (represented with a solid line and dotted line, respectively on Fig. 1). The commutation valves used in this work had an internal volume of $27 \mu\text{L}$ (ref. 161T031). All tubes connecting the different components of the set up were made of PTFE (Omnifit, Cambridge, UK) with 0.8 mm id and end fittings and connectors were also used (Gilson, Villiers-le-Bel, France). The sample loop (SL) and the reaction coil (r) were 800 and 100 cm long, respectively.

A personal computer Pentium II, running SCIWARE (Palmanyola, Mallorca, Spain) Auto-analysis software (version 5.0.3.5) controlled the multi-syringe operation (direction of piston displacement, number of steps and position of all commutation valves).

The spectrophotometric measurements were carried out at the wavelength of 480 and 562 nm for the detection of iron-ammonium thiocyanate and iron-ferrozine complex, respectively. Reference wavelength for minimizing the schlieren effect was set at 700 nm . As detection system, an Ocean Optics PC2000-ISA (Winter Park, USA) spectrophotometer, a pair of $200 \mu\text{m}$ fiber optic cable, a DH-2000

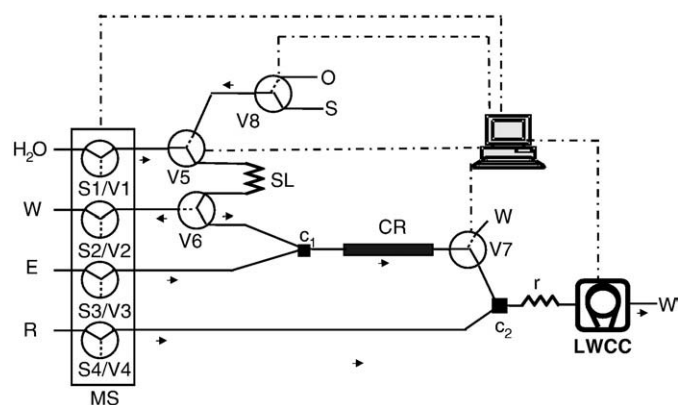


Fig. 1. Multi-syringe flow injection analysis manifold for the determination of iron in waters. S_i: syringes; V_i: solenoid valves in position “on” (discontinuous line) or “off” (continuous line); SL: sample loop (4 mL); r: reaction coil (100 cm); c₁: confluence; LWCC: detector (100 cm optical path, 480 and 562 nm for ammonium thiocyanate and ferrozine, respectively); MS: multi-syringe module; CR: chelating resin (NTA Superflow 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).

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