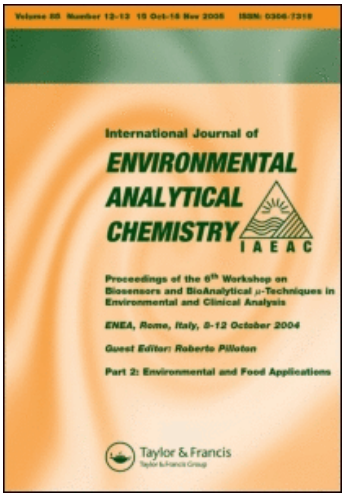

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A miniaturized flow-injection analysis (μFIA) system with on-line chemiluminescence detection for the determination of iron in estuarine water

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A miniaturized flow-injection analysis (μFIA) system with on-line chemiluminescence detection for the determination of iron in estuarine water

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A miniaturized flow-injection analysis system constructed from a glass base plate and polydimethylsiloxane (PDMS) top plate was employed for the determination of iron in river water. Two designs were investigated, one utilizing a syringe pump and the other utilizing EOF pumping with a mini-filtration system incorporated. The syringe pump system was used to optimize the analytical method on chip, where the pump was used to deliver both the analyte and the reagents to the reactor chip. The highly sensitive chemiluminescence reaction between alkaline luminol (3-aminophthalhydrazide) and 0.1 M of hydrogen peroxide (H_2O_2) in the presence of iron(II) was utilized. The bright blue light ($\lambda_{max} \sim 440$ nm) emitted was detected using a miniaturized photomultiplier tube interfaced directly under the chip. The light intensity signals were recorded, and the corresponding concentration of iron(II) concentration was determined. The calibration for iron(II) standards was linear up to 0.75 $\mu g\,mL^{-1}$ ($y = 5.7839x + 0.0378$, $r^2 = 0.9939$) with a precision value of up to 3.72% RSD, for $n = 3$. The limits of detection (blank + $3s_{y/x}$) were found to be 28 $ng\,mL^{-1}$. The system which utilized EOF pumping and incorporated a minifiltration unit provided a linear calibration for 0–5 $\mu g\,mL^{-1}$ ($y = 3.316x + 0.1831$; correlation coefficient, $r^2 = 0.9996$) over a working range of 0.0–0.5 $\mu g\,mL^{-1}$. This system provided lower limits of detection 5.1 $ng\,mL^{-1}$ and better repeatability (%RSD less than 0.5% for $n = 4$), but problems occurred with the mini-filtration system at higher iron(II) concentrations. The EOF pumping system provided slightly higher results for the concentration of iron(II) in the Humber estuary (0.058 $\mu g\,mL^{-1}$), but these results were in line with the results expected by the Environment Agency.

Keywords: μFIA system; Chemiluminescence; Luminol; Hydrogen peroxide; Iron; River water; Electro-osmotic pumping and filtration device

1. Introduction

The analysis of transition metals is considered one of the main challenges for researchers in analytical chemistry, environmental science, and medicine. There are many well-established analytical approaches for their analysis, e.g. FAAS, ICP-OES, and ICP-MS, but chemiluminescence is also an accepted approach despite the limited

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number of suitable reactions. This could be attributed to the advantages offered, including high sensitivity, wide determination range, inexpensive reagent and apparatus, easy and rapid measurements, robustness, portability, low contamination risk, and redox speciation capability [1, 2]. Chemiluminescence can be defined as the production of light by a chemical reaction. A flow-injection analysis (FIA) system incorporated with CL detection has proved to be a useful tool for the analysis of metal ions [3, 4]. Iron is considered a major component of the earth's crust [5]. It plays an important role in oceanic biogeochemistry and is an essential micronutrient for biological organisms. In certain high nutrient, low-chlorophyll areas of the world's oceans, iron is known to limit biological activity, e.g. the phytoplankton growth [2, 6, 7], which otherwise may endanger the global carbon cycles [5]. Despite its enhanced abundance in the earth crust, its concentration in the oceans is very low (<2 nM) [2, 5].

The last two decades witnessed significant developments in the techniques used for the analysis of dissolved iron in seawater, this comes as a part of efforts to reach a better understanding of the role of iron in biological activities [2]. Iron can exist in three oxidation states; neutral (0), (II), and (III). Fe(II) and Fe(III) are involved in the formation of soluble and insoluble inorganic complexes, colloids and particulate phases [2, 8–10]. Mulaudzi *et al.* [11] employed a spectrophotometric sequential injection system for the on-line determination of iron(II) and iron(III). A quantitative discrimination of two iron species was possible with %RSD of 0.8 and 1.3, respectively. The detection limit obtained was found to be 0.1 and 0.15 $\mu g\,mL^{-1}$ for Fe(III) and Fe(II), respectively. O'Sullivan *et al.* [12] developed a highly sensitive method for the determination of Fe(II) and reducible iron in seawater at subnanomolar levels by using a stopped flow luminol chemiluminescence method. Here, the oxidation of Fe(II) by O_2 in the absence of H_2O_2 was used to catalyse luminol chemiluminescence reaction. The typical flow-injection chemiluminescence (FI-CL) manifolds used for the analysis of iron in seawater incorporated an on-line preconcentration column such as an 8-hydroxyquinoline (HQ) microcolumn to improve the limits of detection. A high-voltage photomultiplier tube (PMT) was typically used for the detection, although a low-power (5 V) miniature photon counter has been used as well [13]. Obata *et al.* [14, 15] used hydrogen peroxide as an added oxidant to determine iron(III). The sample was acidified to pH 3.0, and iron(III) was selectively preconcentrated on an 8-HQ column prior to its detection. To determine iron(II) using the same column, initial removal of iron(III) from the sample was required. The sample pH was increased to 6 for the preconcentration of iron(II). Bowie *et al.* [5] and Powell *et al.* [16] exploited the iron(II)-catalysed oxidation of luminol by dissolved oxygen present in the reagents to selectively determine iron(II) [17–20]. Iron(III) was reduced to iron(II) using sodium sulfite, then preconcentrated on-line using an 8-HQ microcolumn before finally measuring the total dissolved iron in the unfiltered samples. The detection limit ($3s$) was 40 pM when 1.5 mL was loaded onto the column, and the precision was 3.2%, RSD ($n=5$) for a 1.0 nM Fe sample. Croot and Laan [21] reported a method for the continuous determination of Fe(II) in polar waters. Surface seawater was pumped into a shipboard clean room container using a towed stainless steel sampling fish. Fe(II) was determined by flow-injection analysis using a modified FeLume. The FeLume system, which was developed by King [22], is an automated FIA system where the reaction takes place in a spiral flow cell in front of the photomultiplier/photon counter. The seawater was filtered in-line, and the sample containing Fe(II) was mixed with luminol

inside a flow cell. A photon counter linked to a PC unit was used to measure the luminescence signal. The detection limit obtained after spiking the solution with known concentrations of Fe(II) ranged from 25 to 133 pM.

In this article, we detail a miniaturized FIA system constructed from glass and polydimethylsiloxane (PDMS) and interfaced with an on-line chemiluminescence detector for the determination of iron(II) in river water. A pulse-free flow delivery system has been used to deliver both the analyte and the luminol-peroxide mixture to the reactor chip. A microporous silica frit was employed as a filtration and pumping device to deliver the analyte to the reactor chip by the application of an electrical field to give electro-osmotic pumping. The system was based on the Fe(II)-catalysed oxidation of luminol by hydrogen peroxide emitting a blue light ($\lambda_{max} \sim 440$ nm). The light was detected on-line by a miniaturized PMT positioned under the chip. The signals obtained were recorded then converted afterwards to the corresponding concentration of iron(II). Studies have been conducted to investigate the impact of using a syringe pump for the delivery of analyte and reagents to the μFIA system compared to a gravity-based pump on both the detection limit and precision values for the determination of iron in river water by using our proposed μFIA system.

2. Experimental

2.1 *Reagents*

All the reagents and standards were of analytical grade unless otherwise stated, and all the dilutions have been carried out with ultra-high-purity (UHP) de-ionized water (18 MΩ cm^{-1} resistivity).

A 0.1 M carbonate buffer solution was prepared by dissolving 5.3 g of Na_2CO_3 (99%, supplied by Riedel-deHaën, Germany) in 500 mL of UHP water, and the pH of the solution was adjusted to 10.5 by the addition of 0.1 M sodium hydrogen carbonate (prepared by dissolving 4.2 g of $NaHCO_3$, supplied by Fisher Scientific Co., Loughborough, UK, in 500 mL of UHP water), and the final dilution was made to 1 L.

A 0.01 M solution of Luminol (3-aminophthalhydrazide, supplied by Fluka, Chemie GmbH, Buchs, Switzerland) was prepared by dissolving 0.177 g of luminol in 100 mL of carbonate buffer pH 10.5) followed by sonicating for 30 min. The solution was kept refrigerated for 24 h prior to using in order to obtain a maximum and stable sensitivity for an optimum chemiluminescence reaction. Luminol solutions are stable for at least 1 month [5].

Hydrogen peroxide solution (0.1 M), was prepared by the dilution of 1.12 mL of H_2O_2 (>30% (w/v)), supplied by Fisher Scientific (Loughborough, UK) with 100 mL of UHP water. This solution was used as an oxidizing agent for luminol.

A 1000 μg mL^{-1} standard solution of iron(II) was prepared by dissolving 0.7022 g of ammonium iron(II) sulfate $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, (supplied by Riedel-deHaën, Germany) in 100 mL of UHP water. Serial dilutions of the stock 1000 μg mL^{-1} solution were then carried out to prepare a range of working standards from 0.05 to 10.0 μg mL^{-1}. These solutions were stored at 4°C in polyethylene bottles.

A 0.1 M solution of high-purity HCl (supplied by Romil SPA pure Chemistry, Cambridge, UK) was prepared by making the necessary dilution to 100 mL with UHP water, to be stored afterwards in a polyethylene bottle.

2.2 *Preparation of electro-osmotic pumping device*

To construct the electro-osmotic pumping device, a microporous silica frit was fabricated following a modified procedure reported by Wilson *et al.* [23]. A 100 μL aliquot of formamide (98%, Avocado Research Chemicals Ltd, Heysham, UK) was mixed thoroughly with 400 μL of distilled water and a 700 μL aliquot of potassium silicate (21% SiO_2, 9% K_2O, Prolabo, Manchester, UK). The homogeneous mixture was then drawn into 10-cm capillary tubes of 1.5 mm i.d. by means of a peristaltic pump set at minimum pump speed (0.25 μL min^{-1}). The tubes were closed at one end, and allowed to stand vertically in an oven set at 60°C for 1 h. After cooling, the tubes were cut into 2-cm-long pieces and washed sequentially with phosphate buffer solution (0.1 M, pH 5), UHP water, 10% (v/v) of hot HNO_3 solution (AR grade), and finally UHP water. Thorough washing of the frit is important to remove any unreacted reagent that could possibly block the frit after rehydration [24]. The washed frits were then returned to an oven set at 80°C and left there overnight for complete dryness. The frit units were stored in a desiccator to maintain their dryness until required.

2.3 *Construction of the μFIA system with on-line chemiluminescence detection*

Figure 1 shows a schematic diagram of the system. The chip was fabricated according to a previously reported methodology [25] with the channel network etched into a glass base plate and the reservoirs located in a removable polydimethylsiloxane (PDMS) top plate. The glass base plate (Photonics, UK) was coated with a layer of chromium

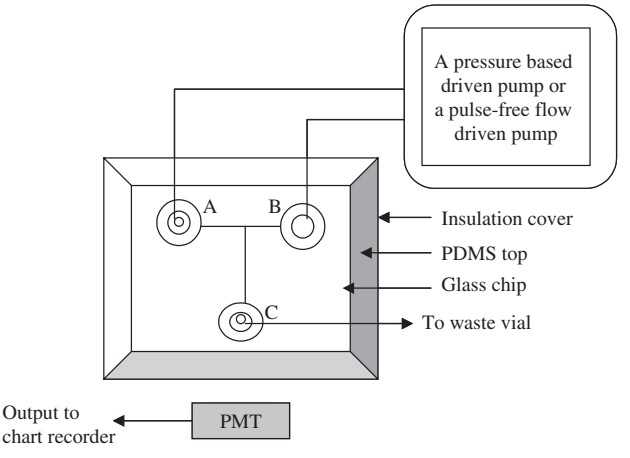

Figure 1. Schematic diagram for the chemiluminescence-based μFIA for the determination of iron(II) and iron(III) in river water. Each intersecting channel in the glass chip was etched with a length of 20 mm, width of 200 μm, and depth of 50 μm. The positions of the reservoirs were labelled A–C. Reservoir A resembled reservoir C in size; each was made with a diameter of 0.5 mm for its bottom half and 1.5 mm for its top half. Reservoir B was made with a diameter of 1.5 mm. A 0.5-mm-diameter draining channel was moulded with the sidewall of reservoir C.

and photoresist. It was photolithographically patterned then etched in 1% hydrofluoric acid/ammonium fluoride for 10 min at 60°C. The glass chip consisted of two intersecting channels forming a T-pattern; each channel was 20 mm long, 200 μm wide, and 50 μm deep.

The positions of the reservoirs were labelled A–C. The top plate was made from PDMS (Stourbridge, UK), which was prepared according to the manufacturer's instructions, vacuum-degassed, and then moulded with the reservoirs in place. Reservoir B was 1.5 mm i.d. to allow a PTFE tubing connected to a stop-flow miniature valve to be fitted. The diameter of reservoir A changed part way down the structure. The top half was 1.5 mm i.d., thus allowing the frit unit to be secured in the reservoir with a platinum electrode (cathode) being positioned so that it directly faced the lower end of the frit unit. The lower part of reservoir A was 0.5 mm in diameter to reduce the dead volume after the frit. The anode (a platinum electrode) was located at the upper face of the fritted capillary. The voltage was applied across the electrodes, and the internal currents generated within the samples were monitored using an AVO digital autoscaling multimeter (Thurnby Thunder Instruments, Huntington, UK) connected in parallel with the device. Reservoir C resembled reservoir A in size, and this was used to drain the μFIA system of waste solutions by directing it to the waste vial via a 0.5-mm-diameter draining channel moulded with the sidewall of the reservoir. The two halves of the microreactor were held together by a simple perspex clamp with four corner bolts to apply pressure. A thin rubber gasket cut from a suba-seal was inserted between the reservoirs inlets and the perspex clamp in order to prevent any possible seeping from reagents and/or analyte to the system top that could result from the PDMS expansion. The miniaturized system could easily be disassembled for cleaning whenever required.

Two types of solvent-delivery system were investigated. To optimize the system, a syringe pump (Bioanalytical Systems Inc., model MD-1001, West Lafayette, IN) was used for both reagents and analytes. At a later date, a mixture of gravity feed and EOF as described above was utilized.

A miniaturized PMT (Hamamatsu Photonics, Enfield, UK) contained in a custom-built, light tight, insulation box and connected to a dual power supply (RS Components, Corby, UK) was located under the lower face of the miniaturized system (glass chip) such that it would be exposed directly to the light emitted during the chemiluminescence reaction. The edges of the chip were covered with black insulation tape to minimize light scattering, and all the operation tests were conducted in a dark room and away from any outside light source. The analogue output from both the PMT detector and the dual power supply was connected to a chart recorder (Chessel BD40-04, Kipp & Zonen, Netherlands) where the CL emission intensity signals were recorded.

The luminol chemiluminescence reaction is shown in figure 2. Several oxidizing agents can be used, including hydrogen peroxide and oxygen. If hydrogen peroxide is used, an initiator or co-oxidant is required, and in particular transition metals have been utilized, including Fe(II) [26]. A three-step mechanism for the reaction in aqueous media has been suggested by Merenyi *et al.* [27]. The first step involves the oxidation of the luminol to produce a luminol radical, followed by the oxidation of the luminol radical, where the key intermediate produced is thought to be α-hydroxyhydroperoxide. Finally, the intermediate decomposes, and light is emitted at 425 nm. The chemiluminescence is affected by pH, with the efficiency being optimized around pH 10.5.

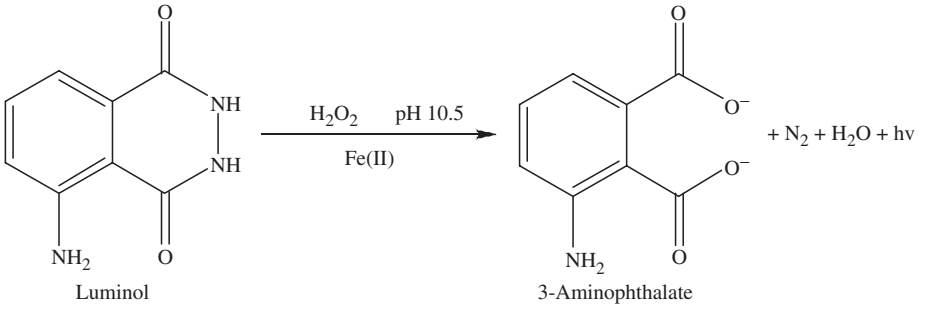

Figure 2. Reaction scheme of iron(II) catalysed oxidation of luminol by hydrogen peroxide.

3. Results and discussion

3.1 *Optimization tests for the chemiluminescence detection of Fe(II) in river water using a syringe pump as a pulse-free flow delivery system for reagent and analyte*

For initial investigations a syringe pump was used to deliver both the reagent mixture (luminol/hydrogen peroxide) and Fe(II) standard solutions to the reactor chip. Fe(II) solutions were prepared and loaded into syringe A, while the reagent mixture (luminol/hydrogen peroxide) (1 : 1) was loaded into syringe B. A range of different iron concentrations were examined from 0.05 to 0.5 $\mu g\,mL^{-1}$. PTFE tubing was used to link the syringes to reservoirs A and B, respectively. The pump flow rate was set to 20 $\mu L\,min^{-1}$. Once the reagents and the standard solutions were mixed inside the channel, and while they swept rapidly toward the waste vial via reservoir C, a short-lived bright blue light was produced, and the chemiluminescence was monitored via the PMT positioned under the channel. Initial results produced a very noisy signal due in part to the formation of nitrogen bubbles during the reaction. Also, insufficient mixing of iron(II) standard solutions and reagents in the channel could result in precipitation of Fe(III) hydroxide after the iron(II) was oxidized in the alkaline luminol solution leading to a fluctuation in the CL intensity signals. It was therefore found to be vital to wash the microreactor frequently to prevent any possible problems associated with contamination and precipitation. This was achieved using high-purity 0.05 M HCl, followed by rinsing with UHP water and then priming ready for the next sample with carbonate buffer pH 10.5.

The luminol and hydrogen peroxide reagents were premixed, but it is known that reagent viability changes over time as a result of partial oxidation of luminol by hydrogen peroxide. In this work, the reagent mixture was prepared fresh prior to beginning the measurement process [28]. To investigate the role of Fe(II) on the enhancement of the chemiluminescence intensity signals obtained from the luminol/hydrogen peroxide reaction, a calibration was obtained for a range of Fe(II) standard solutions (0.0–10.0 $\mu g\,mL^{-1}$). After the syringe pump was loaded with the iron(II) standard solutions, the flow rate was reduced to 20 $\mu L\,min^{-1}$ and the delivery process was activated. The calibration was found to be linear in the range of 0.00–0.75 $\mu g\,mL^{-1}$, giving a linear equation of $y = 5.7839x + 0.0378$ with a correlation coefficient of ($r^2 = 0.9939$). The limit of detection was evaluated using the blank + $3s_{y/x}$ (the error

calculated in the y direction) as defined by Miller and Miller [29], and it was found to be $0.028\,\mu g\,mL^{-1}$ with a precision ranging from 0.00 to 3.72% RSD for $n=3$ for the concentration range ($0.00–0.75\,\mu g\,mL^{-1}$). Each sample run was completed in 3 min, after flushing the reactor chip with 0.05 M of high-purity HCl, UHP water and carbonate buffer pH 10.47.

This method was investigated for the analysis of iron(II) in a estuarine water sample. The sample was collected from the Humber Estuary (Hull, UK) in polyethylene bottles and filtered through a Whatman filter paper (No. 541) to remove course sediment before storage at 4°C. The sample was diluted with UHP water (1 : 1) (v/v), and the concentration of iron(II) was found to be $0.032\,\mu g\,mL^{-1}$ with a %RSD of 3.72% (for $n=6$). This value was lower than expected by the Environment Agency results, and this could possibly attributed to the existence of very fine unfiltered particulates in the river water sample affecting the measuring system. This suggests that an efficient filtration device needs to be incorporated with the proposed μFIA system to isolate these fine particulates sufficiently while delivering the sample to the analysis chip. More investigations were required at this stage to increase the sensitivity and reliability of the proposed μFIA system.

3.2 *On-line chemiluminescence detection of iron(II) and iron(III) in river water using gravity and electro-osmotic pumping as a pulse-free flow delivery system for reagent and analyte*

The μFIA system was constructed as discussed in section 2.3. A microporous silica frit along with the application of high electrical field was used as a filtration and pumping device to deliver the analyte to the reactor chip via reservoir A. The microporous frit had pore sizes in the range of 2–10 μm. A gravity-based propelling device was used to deliver the luminol/hydrogen peroxide mixture to the reactor chip via reservoir B. A concentration range of iron(II) ($0.00–10.0\,\mu g\,mL^{-1}$) standard solutions, freshly prepared, were loaded into the sample reservoir while the reagent mixture (luminol/hydrogen peroxide) (1 : 1), was loaded into the reagent reservoir where the flow was induced by gravity and controlled by a miniaturized stop-flow valve. The platinum electrodes were carefully inserted and positioned at the respective ends of the frit unit; an electrical field of 400 V was applied to obtain a typical flow rate of $5\,\mu L\,min^{-1}$. It was necessary to avoid a high voltage since this would burn the frit components. Also, voltages above 400 V tend to form bubbles and lead to Joule heating effects, thus interrupting the analytes delivery to the reactor chip [28]. Sparks have been observed at the electrodes when they were positioned close to the frit, and bubbles evolved from the reagent mixture disrupted the fluid continuity [28]. The reagent reservoir was set at a height of 50 cm to obtain a $20\,\mu L\,min^{-1}$ flow rate for the reagent mixture. Both the reagent and the standard solutions were allowed to flow to the system when both the power supply and the stopped-flow valve were switched on. Once they mixed inside the channel, and as they swept rapidly to the waste vial via reservoir C, a short-lived bright blue light was produced (2.0 s) with the CL emission signals being monitored by a PMT positioned under the channel. Possible effects of contamination and precipitation can be minimized by following a rigorous cleaning process between each analyte injection.

Figure 3 shows the calibration plot of chemiluminescence intensity over a concentration range of iron(II) ($0.00–5.00\,\mu g\,mL^{-1}$). The plot was found to peak at

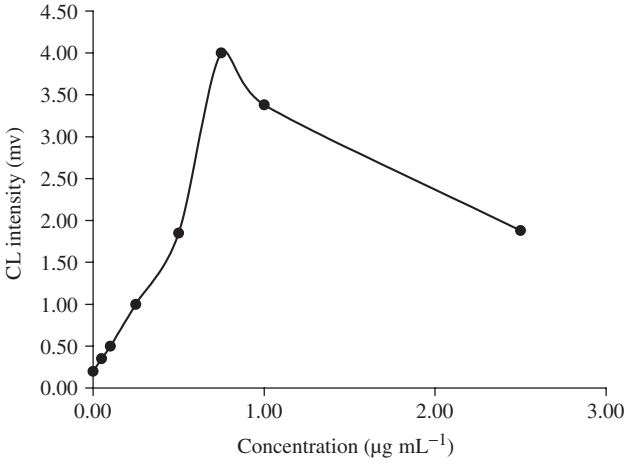

Figure 3. Calibration graph for the CL detection of iron(II) using a μFIA system with pulse-free gravity and EOF driven system.

0.75 $\mu g\,mL^{-1}$, and then a significant decrease in the CL intensities with the increase in iron(II) concentrations was noted. On close observation of the frit system at high iron(II) concentrations, a coloration was seen inside the frit, with a colour change from white to pale yellow. This could be due to oxidation of iron(II) to an iron(III) precipitate or the formation of a complex between iron(II) and the frit composition. This suggests that a further investigation to the frit material is required at this stage to maintain its tolerance to the high concentrations of iron(II).

The limit of detection was found by plotting the linear portion of the graph (0.00–0.50 $\mu g\,mL^{-1}$) with a line equation of $y = 3.316x + 0.1831$ with a correlation coefficient ($r^2 = 0.9996$). The limit of detection was evaluated using the blank + $3S_{y/x}$ (the error calculated in the y direction) as defined by Miller and Miller [29], and was found to be 0.0051 $\mu g\,mL^{-1}$ with a precision of $\leq$(0.5%) RSD for $n = 4$ for the concentration range (0.00–0.50 $\mu g\,mL^{-1}$). Each sample run was completed in 3 min, after flushing the reactor chip with 0.05 M of high-purity HCl, UHP water, and carbonate buffer, pH 10.47.

Interferences to this method have been widely investigated and were not undertaken as part of this study; they are possible via other chemical reactions that can produce O_2^- or oxidize Fe(II) [22]. O'Sullivan *et al.* [12] for instance identified only Cu(II) and Mn(II) as potential metal interferences, as they oxidized Fe(II). Mulaudzi *et al.* [11] noted that copper can cause interference when its concentration rises above half of the total iron concentration. Co(II) can also show a strong positive interference at all concentrations, and it is known to be an efficient catalyst for the luminol CL system according to Klopf *et al.* [18]. Complexation with fulvic and humic acids will also affect the results [26]. This study was however focused on the design and fabrication of a μFIA system for the determination of iron(II) in natural water samples; further interference studies were not carried out.

A sample was collected as described previously from the Humber Estuary (Hull, UK) and analysed using the EOF pumping system. The concentration of iron(II) was found to be 0.058 $\mu g\,mL^{-1}$ with a precision $\leq$(0.5%) RSD for $n = 4$, and this result agreed

with those from the Environment Agency. The results obtained clearly demonstrate that we successfully developed a μFIA system with on-line chemiluminescence detection for the determination of iron(II) river water and without the need for any mechanical devices to deliver the reagents and the analyte. This opens the way for the construction of more portable devices that can be used for water quality control purposes.

4. Conclusions

In this study, a μFIA system for the on-line chemiluminescence detection of iron(II) and iron(III) in river water has been described. A microporous silica frit along with the application of high field strength has been used for the filtration and delivery of the analyte to the reactor chip electroosmotically while the reagent mixture was delivered to the system by gravity. To optimize the proposed μFIA system, a pulse-free flow driven system including a syringe pump, and gravity and EOF pumps for the delivery of analyte and reagent has been investigated. The EOF pumping system gave a better reproducibility at low iron concentrations, but at high concentrations a problem occurred with the frit. This problem was not observed for concentrations of iron(II) below $0.75\,\mu g\,mL^{-1}$.

Under optimized conditions, a river-water sample was analysed, and the concentration of iron(II) was found to be $0.058\,\mu g\,mL^{-1}$ with a precision value $\leq$(0.5%) RSD for $n=4$. This means that a reliable and reproducible system for the determination of iron(II) has been constructed and without the need for any mechanical devices for the sample delivery and filtration. Also, the concentration of total iron obtained from this application was in good agreement with the concentration range of $0.050–0.344\,\mu g\,mL^{-1}$ (provided by the Ridings Environment Agency, Leeds, UK), for the analysis of total iron in different sampling points of River Humber water. Further work is now required to look at iron speciation and automation of the system.

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