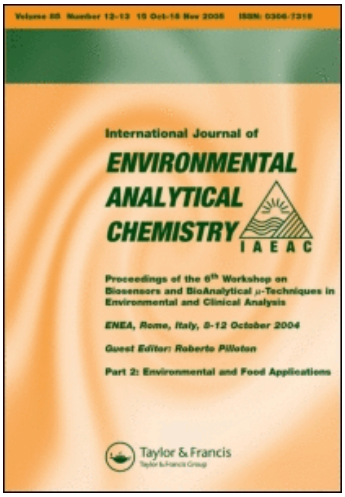

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Flow-injection determination of total iron in freshwater samples with neutralisation chemiluminescence

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Flow-injection determination of total iron in freshwater samples with neutralisation chemiluminescence

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A flow-injection chemiluminescence method has been established for the determination of total iron in freshwater samples. The enhanced chemiluminescence emission was caused by the iron(II) from the neutralisation reaction of hydrochloric acid and sodium hydroxide without the use of any chemiluminescent reagent. The calibration graph was linear in the concentration range of 2.8–560 $\mu g\,L^{-1}$ ($r^2 = 0.9983, n = 8$), with relative standard deviation (RSD; $n = 4$) in the range of 0.8–2.6%. The limit of detection ($S/N = 3$) was 0.56 $\mu g\,L^{-1}$ with injection throughput of 180 h^{-1}. The effect of common anions and cations were studied over their environmentally relevant concentrations in freshwaters. The method was successfully applied to determine total iron in freshwater samples. Iron(III) was reduced to iron(II) by using hydroxylammonium chloride. The proposed method was compared with spectrophotometric method and there was no significant difference between the two methods at the 95% confidence level (*t*-test). Analysis of river water (certified reference material SLRS-4) for iron(II), after reduction of iron(III) with hydroxylammonium chloride, gave good results ($2.17 \pm 0.22\,\mu M$ compared with the certificate value of $1.85 \pm 0.1\,\mu M$).

Keywords: flow-injection analysis; chemiluminescence; neutralisation reaction; iron; freshwater samples

1. Introduction

Iron is the fourth most abundant element in the earth's crust. The main source of iron in natural waters is from the weathering and leaching of rocks and soils. Iron is present as iron(II) and iron(III) states in natural waters, but it is usually in the iron(III) state and its salts are readily hydrolysed to insoluble forms, so the iron concentration in natural waters is generally low [1]. Iron is vital for living organisms, participating in a wide variety of biological processes, including oxygen transport, DNA synthesis and electron transport, and is the most common nutritional deficiency worldwide [2,3]. Excess intake of iron can cause several chronic diseases such as diabetes, cancer and cardiovascular diseases [4–6]. The concentration of iron in freshwater can be found at levels ranging from 10 to 1000 $\mu g\,L^{-1}$ [7] and the recommended limit for filterable iron in drinking water is 300 $\mu g\,L^{-1}$.

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A number of analytical methods for quantitative analysis of iron in various samples have been developed such as UV-Vis spectrophotometry [8–13], atomic absorption spectroscopy [14], inductively coupled plasma atomic emission spectroscopy [15], fluorescence [16], electrochemical [17], high performance liquid chromatography [18], and micro-column ion chromatography with UV-Vis detection [19]. Some of these methods are highly sensitive, however; the disadvantages are necessity of expensive and sophisticated instrumentation, complicated operation system and maintenance.

Nowadays, flow-injection analysis (FIA) methods are applied routinely in laboratories because FIA is often more rapid, sensitive and precise than manual procedures and utilises small sample volume, allowing low reagent consumption and high sampling frequency. Also FIA instruments can easily be carried out during field analysis (i.e. onboard research vessels, for example). Chemiluminescence (CL) reactions are transient in nature and FIA is the most suitable technique for monitoring CL reactions. CL has the advantages of involving simple instrumentation, low detection limits, wide dynamic ranges, high sample throughput and robustness [20]. Several FI-methods with CL detection have been developed for the determination of trace metals in diverse matrices at very low concentrations using various CL reagents [21]. CL methods based on the catalytic effect of iron(II) on the oxidation of luminol with hydrogen peroxide in alkaline medium have been reported [22,23] with detection limits of 0.112 and 2.8 $\mu g\,L^{-1}$ and sampling rate of 18 and 20 h^{-1}, respectively. Both methods involve complicated manifolds and serious interferences from vanadium(IV), chromium(II & VI), manganese (II), cobalt(II) and copper(II). A similar method has been described for iron(II) and Mn(II) determination based on the catalytic effect of luminol oxidation by potassium periodate [24] with a detection limit of 0.003 $\mu g\,L^{-1}$ for iron(II) and sampling rate of 30 h^{-1}. Substantial interference was observed from cobalt(II) at 100 $\mu g\,L^{-1}$ using dual injection valves with four channel manifold. Ferrozine legend for iron(II) has been used for its determination in seawater using spectrophotometric methods [25,26] with detection limits of 0.034 and 0.006 $\mu g\,L^{-1}$ for iron(II), respectively. Copper(I), iron(III), cobalt(II) and nickel(II) did interfere for iron(II) determination. Table 1, gives a comparison among various analytical methods for the determination of iron(II & III) in terms of sample matrix, calibration range, detection limit and sample throughput [11–13,19,22,23,27,28].

In the present study, we report a simple and more specific FI-CL method without using luminescent reagent such as luminol which requires hydrogen peroxide as oxidising agent for the determination of total iron in freshwater samples. The method is based on the neutralisation reaction of hydrochloric acid and sodium hydroxide with injection throughput of 180 h^{-1}.

2. Experimental

2.1 *Reagents and solutions*

All reagents used were of analytical grade, supplied by Merck (Darmstadt, Germany), unless stated otherwise and all solutions were prepared in ultra-high-purity (UHP) deionised water (Elga, Purelab Option, UK). All plasticware used during this work was cleaned by first soaking in detergent for 24 h, followed by HCl 20% (v/v), thoroughly rinsed with (UHP) deionised water and stored in re-sealable plastic bags to prevent contamination. Iron(II) and iron(III) stock solutions (0.01 M) were prepared by dissolving 0.392 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 0.482 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 100 mL of HCl

Table 1. Comparison among several methods for the determination of iron(II & III).

Technique and reaction	Sample matrix	Linear range ($\mu g\,L^{-1}$)	Limit of detection ($\mu g\,L^{-1}$)	Sample rate (h^{-1})	Ref.
FIA-Spec. *N*,*N*-dimethyl-*p*-phenylenediamine – hydrogen peroxide, catalytic reaction	Natural waters	0–2	0.02	20	[11]
FIA-Spec. Pre-concentration with 1-(2-thiazolylazo)-2-naphthol column	Lake and river water	50–1000	15	25	[12]
FIA-Spec. Chlortetracycline reagent, yellow complex	Natural waters	500–20000	100	60	[13]
Spec – Ion chromatography, iron(III)-salicylic acid and iron(II)-1,10-phenanthroline complexes	Fresh water	2500–50000	100	NG	[19]
FIA – Luminol – hydrogen peroxide CL	Natural waters	0.28–56	0.056	18	[22]
FIA – Luminol – hydrogen peroxide CL	River water	0–750	28	NG	[23]
FIA – Potassium Permanganate – formaldehyde CL	Fresh water	11–56	0.056	120	[27]
FIA – Luminol CL	Standards	0.056–56	0.028	60	[28]
FIA – Sodium hydroxide – hydrochloric acid CL	Fresh water	2.8–560	0.56	180	This method

Notes: NG, not given.
FIA-Spec., flow injection analysis-spectrophotometry.
CL, chemiluminescence.

(0.01 M) solution, respectively. Standards were prepared daily in HCl (0.05 M) by serial dilution of the stock solution. Sodium hydroxide stock solution (0.1 M) was prepared by dissolving 0.40 g of NaOH in 100 mL of UHP water and this solution was standardised against primary standard reagent. Working standards of NaOH were prepared daily by serial dilution. Hydrochloric acid stock solution (0.1 M) was prepared by diluting 0.83 mL of HCl (12.07 M) in 100 mL of water and this solution was also standardised against primary standard reagent. Working standards of HCl were prepared daily by serial dilution. Hydroxylammonium chloride stock solution (0.01 M) was prepared by dissolving 0.07 g of NH_2OH HCl in 100 mL of UHP water whenever required and working standards were daily prepared by serial dilution.

Stock solutions (1000 mg L^{-1}) of cations (calcium(II), magnesium(II), nickel(II), cobalt(II), manganese(II), lead(II), chromium(III), copper(II) and zinc(II)) in HCl (0.01 M) and anions (chloride, sulfate, phosphate, silicate, nitrate, nitrite, bicarbonate, fluoride, arsenate and iodide) in UHP water, were prepared from their respective salts. Various working standards were prepared from these stock solutions for interference studies.

2.2 *Instrumentation and procedures*

The flow system used for the determination of iron(II) with CL detection is shown schematically in Figure 1. A peristaltic pump (Ismatec Reglo 100, Switzerland) was used to deliver the sample carrier and the reagent solution at a flow rate of 2.5 mL min^{-1}. A rotary injection valve (Rheodyne 5020, Anachem, Luton, UK) was used to inject iron(II) standards into HCl (0.05 M) stream. This stream was then merged at a T-piece with NaOH (0.025 M) stream. The merged streams were allowed to travel 3.0 cm before passing through a glass spiral flow cell (2 mm i.d., 25 mm dia.) placed directly in front of an end window photomultiplier tube (PMT, 9798B, Electron Tubes, Ruislip, UK). The PMT, glass coil and the T-piece were placed in a home built light-tight housing. The PMT was attached to a 2 kV power supply (Electron Tubes, PM20SN, UK). The PMT output was recorded using a chart recorder (Kipp & Zonen BD40, Holland).

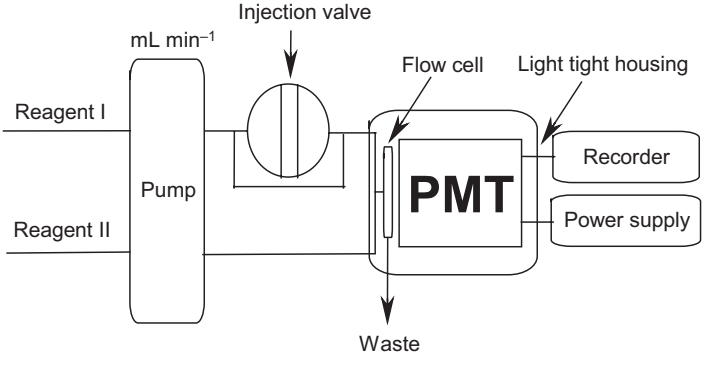

Figure 1. Flow injection manifold with photomultiplier tube detection system. Reagent I = 0.05 M HCl, Reagent II = 0.025 M NaOH, Sample volume = 180 µL, PMT voltage = 1100 V and flow rate = 2.5 mL min^{-1}.

3. Results and discussion

3.1 *Possible CL mechanism*

Neutralisation reactions involving strong acids and bases occur in the presence of molecular oxygen in aqueous solutions, a weak CL emission is emitted in the 400–600 nm region. Generally, it is agreed that the observed CL in this inorganic case has its origin in excited oxygen [29–31]. However, the mechanism of the CL reaction induced by neutralisation is unclear. Inorganic CL reaction systems, which include oxidation reactions such as the reaction of hydrogen peroxide with hypochlorite ion [32], have been extensively investigated. In these cases, excited singlet molecular oxygen dimmers are supposed to be the emitting species produced in the reaction. An increase in the CL emission induced by neutralising nitric acid with potassium hydroxide has been reported [33] when iron(III) (90 μM) was added in acid. In this iron-catalysed CL process, the excited oxygen is supposed to be produced more effectively in a reaction of molecular oxygen with iron-radical complexes formed during neutralisation.

It was reported [33] that iron(III) has greater enhancement effect than iron(II) on CL of nitric acid and potassium hydroxide when compared with other acidic media. It was also studied that hydrochloric acid has suppressed the CL of iron(III) due to the formation of iron(III) – chloride complex. The suppression of CL intensity on the iron(III) enhanced CL from neutralisation reaction by using anions was also reported [34]. In the present study, we have observed that hydrochloric acid (0.05 M) and sodium hydroxide (0.025 M) when used with iron(II) caused greater CL signal as compared with iron(III). This could be due to the availability of chloride ions forming stronger complex with iron(III) which in turn lowers the concentration of iron(III) available to hydrolyse forming hydroxyl complexes and free radicals for CL emission.

The CL response of iron(II) solution (560 $\mu g\,L^{-1}$) in the presence and absence of dissolved oxygen was studied using the proposed FI-CL manifold. In the presence of dissolved oxygen, the response of iron(II) using reagents; HCl (0.05 M, sample carrier stream) and NaOH (0.025 M, reagent stream), a CL signal of 64 ± 0.5 mV ($n = 4$) was obtained. When the dissolved oxygen was removed from the reagent solutions (HCl, NaOH and iron(II)) by purge of nitrogen for 5 min, the CL signal of 14 ± 0.6 mV ($n = 4$) obtained was decreased about 78% which is proportional to the decrease in dissolved oxygen concentration. In contrast, when the solutions were purged again with oxygen, the CL signal of 67 ± 1.2 mV was restored. This study indicates that the dissolved oxygen plays an important role in the iron(II) catalysed CL process of neutralisation reaction of HCl with NaOH.

In order to examine if the reactive oxygen species participated in the CL reaction, the scavengers of reactive oxygen species, such as ascorbic acid, sodium benzoate and mannitol, were added into the reagent solutions. The CL intensity was decreased greatly in the presence of these scavengers of radical. These results showed that there is reactive oxygen species in the CL neutralisation reaction.

3.2 *Optimisation of FI manifold*

In order to establish the optimum conditions for the determination of iron(II), various experimental parameters were investigated using a univariate approach. The key parameters optimised were sodium hydroxide, hydrochloric acid concentrations, the sample volume and the flow rates. For the reduction of iron(III) to iron(II), hydroxylammonium chloride

concentration was also optimised. All of these studies were performed with iron(II) standard solution 0.1 μmol L^{-1} (60 μL) and a PMT voltage of 1100 V.

3.2.1 *Effect of mineral acids*

The effect of H_3PO_4, HNO_3, $HClO_4$, H_2SO_4 and HCl were investigated on the determination of iron(II). An increase in CL intensity was observed when using $H_3PO_4 < HNO_3 < HClO_4 < H_2SO_4 < HCl$ as a sample carrier stream. The CL response of HCl was higher than the other mineral acids studied and therefore, chosen for subsequent experimental studies. The effect of HCl concentration was then investigated in range of 0.01–0.1 M. An increase in the CL intensity was observed from 0.01–0.05 M and further increase in HCl concentration resulted in decrease in CL response (Figure 2a). The enhancement effect of chloride ions on luminol CL reaction has also been reported

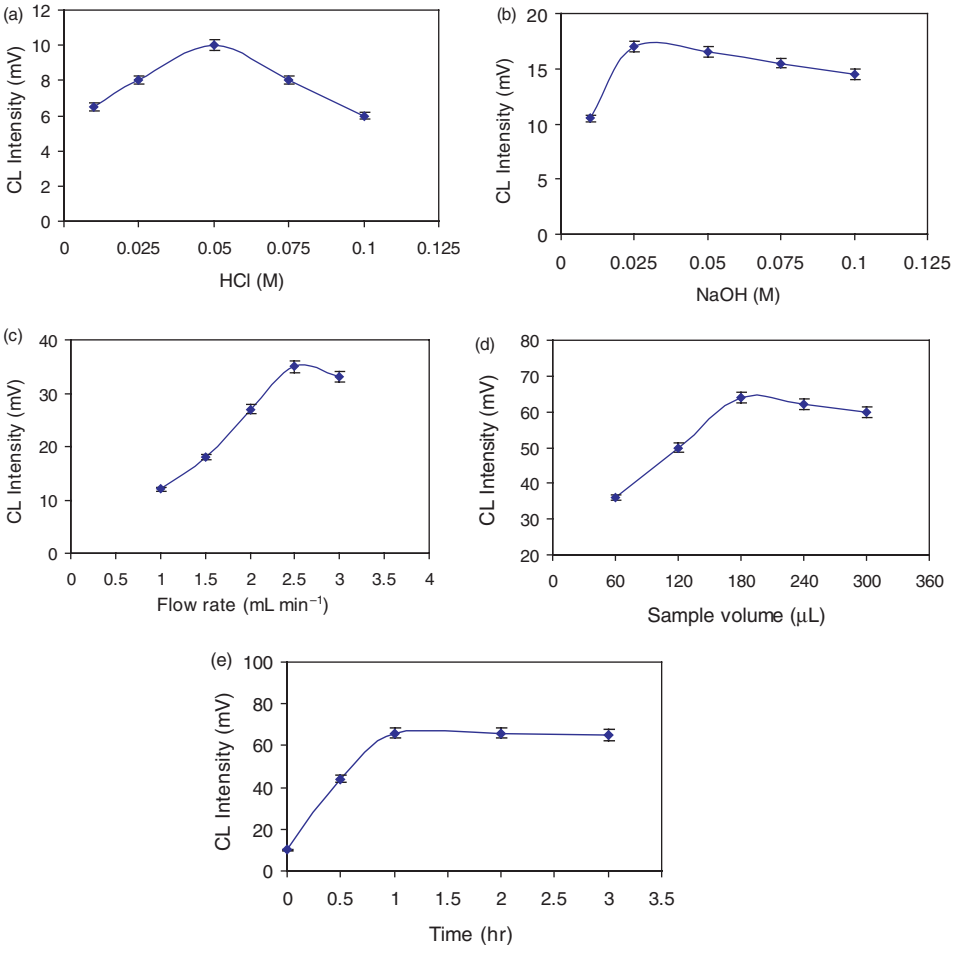

Figure 2. Variation of CL intensity with: (a) HCl and (b) NaOH concentrations (c) flow rate for sample carrier and reagent streams, (d) sample volume and (e) time profile of hydroxylammonium chloride for reducing iron(III) to iron(II).

previously [35,36]. Therefore, HCl concentration of 0.05 M was selected and used subsequently. Blank values for these mineral acids was also investigated on the iron(II) determination by injecting water as a blank and observed negligible CL responses.

3.2.2 *Effect of sodium hydroxide*

The influence of NaOH concentration was studied over the range of 0.01–0.1 M using optimised HCl conditions. The CL response increased up to 0.025 M NaOH, above which the NaOH had little effect on the CL (Figure 2b). Therefore, 0.025 M of NaOH was selected as optimum for subsequent experiments. The pH of NaOH (0.025 M) and HCl (0.05 M) when measured from the waste was acidic. This clearly indicated that CL from the neutralisation reaction requires acidic media.

3.2.3 *Effect of flow rate and sample volume*

The optimum concentration of reactants in a flow-injection analysis is a matter of matching the rate of reaction to the flow rate so that the maximum emission occurs during the transit of the sample through the flow-cell. The flow rates for each of two channels were simultaneously investigated over the range 0.5–3.5 mL min^{-1} in terms of the sensitivity, the reagent consumption and the sample throughput. A flow rate of 2.5 mL min^{-1} gave maximum CL response (Figure 2c) with a steady base line and reproducibility of ($<2.0\%$ RSD). Above a flow rate of 2.5 mL min^{-1}, CL intensity was decreased.

It is well known that the sample injection volume in a flow-injection set-up affects the signal intensity. An increase in sample volume normally leads to an increase in the emitted CL signal. A sample injection volume of 180 μL gave maximum CL signal (range studied 30–300 μL) and was used for further studies (Figure 2d).

3.2.4 *Effect of hydroxylammonium chloride for reduction process*

Total dissolved iron concentration can be determined by reducing iron(III) to iron(II) prior to analysis. For reduction process, under selected conditions, different reducing agents including; $SnCl_2$, Na_2SO_3 and $NH_2OH \cdot HCl$ were examined. Among these, hydroxylammonium chloride gave best response due to its rapid and efficient reducing power. Therefore, hydroxylammonium chloride concentration over the range of 1.0–100 μM was investigated. The concentration of 50 μM gave the maximum ($>90\%$) reduction. Therefore a concentration of 50 μM of hydroxylammonium chloride was selected for subsequent experiments. Similarly the time profile of the reducing agent with the optimum concentration was examined. Since the CL response increased with time and was constant after 1 h (Figure 2e). Therefore, a reduction time of 1 h was used for conversion of iron(III) to iron(II).

3.3 *Analytical figures of merit*

The calibration curve of CL intensity *versus* iron(II) was linear over the concentration range of 2.8–560 μg L^{-1} with correlation coefficient (r^2) 0.9983 ($n=8$) and the regression equation $y=6.31x+0.4749$ [y = CL response (mV) and x = concentration (μg L^{-1})]. The relative standard deviation was 0.8–2.6% ($n=4$) over the range studied. The limit of detection ($S/N=3$) was 0.56 μg L^{-1} with injection throughput of 180 h^{-1}.

Table 2. Effect of various ions on the determination of iron(II). All readings are the mean of four injections (blank value = 0.02 mV).

Ions	Concentration ($\mu g\,L^{-1}$)	CL signal without Fe(II) (mV)	CL signal with Fe(II) (mV)	Parametric values* ($\mu g\,L^{-1}$)
Iron	56	0.02	7.0	300
Magnesium	20,000	0.02	7.0	30,000
Calcium	2,00,000	0.04	7.0	1,00,000
Lead	1000	1.0	7.0	10
Nickel	1000	4.0	8.0	20
Cobalt	10	0.03	7.0	1.0
Zinc	1000	4.0	8.0	3000
Chromium	500	0.02	7.0	50
Copper	10	0.01	7.0	2000
Manganese	50	0.02	7.0	50
Phosphate	1000	0.03	7.0	100
Sulfate	2,00,000	0.04	7.0	2,50,000
Chloride	2,00,000	0.02	7.0	2,50,000
Nitrate	10,000	0.01	7.0	10,000
Nitrite	100	0.03	7.0	100
Arsenic	10	0.04	7.0	10
Fluoride	1000	0.03	7.0	1500

Notes: *World Health Organization and European Commission Council Directive (98/83/EC) guidelines for drinking water quality, 1993 and 1998, respectively.

3.4 *Interferences*

The effect of potential foreign ions on the blank response (in the absence of iron(II)) and on the determination of iron(II) (at $56\,\mu g\,L^{-1}$) is shown in Table 2. Interferences include major freshwater ions at environmentally relevant concentration. Majority of the cations and anions do not interfere under the proposed conditions. It has been reported previously [33] that iron(II & III), aluminum(III), chromium(III), copper(II), manganese(II), nickel(II), zinc(II) and cobalt(II) give positive CL response with neutralisation reaction between nitric acid and potassium hydroxide.

3.4.1 *Accuracy*

The accuracy of the proposed method was ascertained by analysing SLRS-4, certified river water obtained from the National Research Council of Canada. This solution was analysed using the proposed FI-CL method after addition of high purity hydroxylammonium chloride solution (50 μM) for one hour at room temperature (25°C) to reduce iron(III) to iron(II). A value of $2.17 \pm 0.22\,\mu M$ was obtained for iron(II) which is in good agreement with the certified value of $1.85 \pm 0.1\,\mu M$.

3.5 *Application to freshwater samples*

The proposed method was applied to the determination of total iron in freshwater samples. Samples were collected from various locations of Quetta Valley, into acid washed high density polyethylene bottles. After collection, samples were filtered through Whatman filter paper No. 42 and samples were acidified (0.05 M HCl). Prior to analysis, the 0.05 mL of hydroxylammonium chloride (50 μM, reducing agent) was added to 100 mL acidified

Table 3. Determination of total iron in freshwater samples by the proposed FI-CL method and spectrophotometric method [37].

Samples	Total iron found ($\mu g\,L^{-1}$)	
	Proposed FI-CL method	Spectrophotometric method
1	22.4 ± 0.4	22.8 ± 0.2
2	19.6 ± 0.4	20.2 ± 0.5
3	22.0 ± 0.3	21.2 ± 0.4
4	23.5 ± 0.4	22.8 ± 0.2
5	24.2 ± 0.2	23.6 ± 0.5
6	25.8 ± 0.3	25.2 ± 0.2

Note: All readings are the mean of four injections.

samples and allowed for 1 h to stand for the reduction of iron(III) to iron(II) and then injected directly into the FI-CL manifold. The results obtained for the six samples (ranges 19.2 ± 0.2–$25.8 \pm 0.3\,\mu g\ L^{-1}$ total iron) and the results obtained by using the spectrophotometric method [37] are given in Table 3. The comparison of two methods for measuring total iron concentration in six freshwater samples was performed using student's *t*-test based on individual differences between results for each sample. It was found that $t_{calculated}$ (1.13) is less than t_{table} (2.571) for 95% confidence and 5 degrees of freedom. The two methods are not significantly different at the 95% confidence level.

4. Conclusions

The proposed FI-CL method for the total iron determination is simple and characterised by high throughput (180 injections h^{-1}), wide dynamic range (2.8–560 $\mu g\,L^{-1}$) and low detection limit (0.56 $\mu g\,L^{-1}$) without the use of CL reagent. Common interferences present in freshwater at their normal concentration levels had no significant effect. Iron(III) was successfully reduced to iron(II) by using hydroxylammonium chloride. The method was applied to the freshwater samples and the results obtained are in good agreement with those obtained by spectrophotometric method. There was no significant difference between the two methods at the 95% confidence level. The method was validated by determining total dissolved iron in certified reference river water (SLRS-4) after reduction with hydroxylammonium chloride. The result, $2.17 \pm 0.22\,\mu M$ was in good agreement with the certified value $1.85 \pm 0.1\,\mu M$.

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