Introduction

Iron, an element commonly present in water environments, is essential for many living creatures. It can reach water systems through several natural and anthropogenic sources, including natural leaching of minerals from soil, industry, and farming activities. Iron ions commonly exist in two oxidation states, the ferrous ion (Fe²⁺) and the ferric ion (Fe³⁺). Of these, the ferrous form is considered to be more toxic. Thus, speciation methods for iron analysis are critical for the accurate monitoring of different iron states in environmental and biological systems. In natural water sources, iron is generally found as Fe³⁺, which at high concentrations can cause a brown appearance and an unpleasant smell. However, Fe²⁺ and Fe³⁺ are present in natural water, and the ratio of both ions depends on redox potential of the system.¹ Additionally, under conditions such as flooding or low dissolved oxygen levels or an anaerobic condition, the potential of toxic Fe²⁺ may accumulate.² This process results in high concentrations of iron in soil, and the potential redistribution of iron into natural waters and paddy fields. This can have a profound effect on agricultural efforts, such as rice production. In countries such as Thailand, where rice agriculture is dependent on natural water conditions, elevated concentrations of toxic Fe²⁺ would impair rice harvests.³ Indeed, there is a clear need for the regular monitoring of iron species in order to examine the equilibrium of iron in natural water. Such assessments would need to be carried out either in fields or immediately after collecting samples, because Fe²⁺ tends to rapidly oxidize and become Fe³⁺.

There are numerous analytical techniques used for iron speciation, such as ion chromatography,⁴–⁹ flow-based analysis,¹⁰–¹⁵ solvent extraction and flame atomic absorption spectrometry (AAS),¹⁶ voltammetry,¹⁷–¹⁹ and fluorescence spectrophotometry.²⁰ However, apart from some flow-based analysis systems, these techniques are infrequently used in field work due to the instrument size and a non-portable nature. Routine techniques for the analysis of iron in either water or waste water samples¹⁸ include AAS and inductively coupled plasma (ICP) spectroscopy. However, these techniques usually quantify only the total iron concentration. In contrast, UV-visible spectroscopy using 1,10-phenanthroline (Phen) is widely used to detect Fe³⁺ specifically. Worsfold et al.²² reviewed the most utilized methods for the analysis of dissolved iron in seawater.
and recommends that for a precise speciation analysis of Fe\textsuperscript{2+}, the analysis must be carried out either immediately after sampling or with samples stored in buffered solutions at a pH of less than 7.2, or at 2 – 4°C.

Research towards green analytical chemistry (GAC) has increased significantly in the past two decades.\textsuperscript{23,24} GAC research focuses on the replacement of toxic reagents, the reduction of reagent consumption, and the minimization of waste generation. A particularly useful strategy for accomplishing these goals is to produce miniaturized analytical systems, such as lab-on-a-chip (LOC) devices or micro total analysis systems (\(\mu\)TAS). A plethora of miniaturized analytical systems, based on the LOC concept,\textsuperscript{25,26} have been described, incorporating such functions as integrated sample injection, sample preparation, and chemical separation and detection. Indeed, such devices have enormous applications in various fields, such as bioassays\textsuperscript{27} and diagnosis,\textsuperscript{28} forensics,\textsuperscript{29} environmental monitoring,\textsuperscript{30–33} and pharmaceuticals and supplement research.\textsuperscript{34–36}

Many of the miniaturized analytical systems developed for heavy metal monitoring use micro-flow analysis (\(\mu\)FA), and include a sample injection, perform on-chip reactions taking place in a microchannel network, and contain chip-based detection capabilities.\textsuperscript{30,31} Perhaps due to the limited size of microchips and the intrinsic problems in sample and reagent manipulation, only a few \(\mu\)FA systems have been designed for the simultaneous analysis of multiple analytes. Moreover, most of these systems rely on a single detection channel due to the high cost of commercial optical detectors and the limited space on microdevices. In this work, LOC technology has been used to design and fabricate a miniaturized analytical device that enables the simultaneous detection of two analytes. To enable multi-analyte detection, this microfluidic device contains microchannel networks fabricated onto two sides of a single substrate along with dual house-made optical sensors for monitoring multiple signals. For proof of concept, the miniaturized system was used to simultaneously measure iron ions using simple colorimetric reagents (Phen and KSCN for Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, respectively.)

**Experimental**

**Fabrication of double-sided microfluidic system (DSMs)**

The base substrate for microchip fabrication was a square (30-mm length, 30-mm height, and 5-mm thick) polymethylmethacrylate (PMMA). Microchannel networks (250 \(\mu\)m \(\times\) 100 \(\mu\)m cross-section) were etched at a rate of 100 mm s\(^{-1}\) into both substrate surfaces using a CO\(_2\) laser (Laser1325, CNCBro, China) operated at 10% power. The device was then sandwiched between two 2-mm thick polydimethylsiloxane (PDMS) sheets so as to enclose the microchannel networks (Figs. 1(b) - 1(c)). The layers were clamped with additional PMMA substrates to both prevent solution leakage and also provide support for dual optical sensors. A schematic of the system is illustrated in Fig. 1.

A multi-syringe pump (LSP10-1B, Longer Pump, China) housing three 5-mL syringes (Nipro, Thailand) was used to
pump solutions and samples through 0.25-mm i.d. PTFE tubing (VICI, USA) and into the microfluidic device. The sample was injected into a carrier stream of DI water using a 6-port valve (Ogawa, Japan, labeled S in Fig. 1) with a sample volume of 10 μL. The other two syringes delivered KSCN (labeled R1 in Fig. 1) and Phen (labeled R2 in Fig. 1) reagents for the analysis of Fe³⁺ and Fe²⁺, respectively. After the microchannels were filled with reagents, the 6-port valve was used to inject the sample into the carrier stream. The stream was then split, and the sample entered both sides of the device where it mixed with reagents present in the microchannels (Fig. 1(a)). A graphic illustrating the channel design in the upper chip section is presented in Fig 1(b). Here, analyze (Fe²⁺) enters the chip through C1 and mixes with reagent flow from R1 (SCN) to produce a red complex (red line) in the microreactor. Flow continues through the cell and exits into the waste (W). The red-colored reaction product flows through the detection cells (1 mm i.d. × 4 mm depth) on both sides, and is monitored utilizing dual optical sensors made in-house.

Sensors consisted of two pairs of 5-mm light-dependent resistors (Silonex USA, TO-18 Photocells, LDR) and 3-mm ultra-bright green-light (λ 583 nm) emitting diodes (T-1, 1440, Ultra-bright LED, Avago Technology). The colorimetric circuit was interfaced with an analog input module (AI210, Wisco, Germany) and a signal presented as mV vs. seconds was collected every 0.5 s. Data was subject to an EDAQ program for evaluating peak height and increasing signal-to-noise ratio via smoothing algorithms in order to increase the sensitivity.

A UV/Vis Spectrophotometer (UV1700, Shimadzu, Japan) was used for batch colorimetry analyses. An ICP atomic emission spectrometer (ICP-AES, 3000, Perkin-Elmer, USA) was used to determine the total Fe in water samples.21

Chemicals
PDMS was prepared using Sylgard 184 (Dow Corning, USA), and consisted of a silicone elastomer and a silicone curing agent mixed at a 10:1 ratio. All other chemicals used in this work were of AR grade. Deionized (DI) water was from an Elgastat UHQ PS water purifier (Elga, England). A 0.1 mol L⁻¹ solution of a 1,10-phenanthroline solution (Phen, Merck, Germany) was prepared by dissolving 0.9912 g in 50.0 mL of DI water. A potassium thiocyanate (KSCN, Merck, Germany) solution at 0.1 mol L⁻¹ was prepared by dissolving 0.9718 g in 50 mL of DI water, and making up to 100.0 mL.

A 1 g L⁻¹ stock solution of Fe²⁺ standard was prepared by dissolving 0.3514 g of ammonium ferrous sulfate hexahydrate (Merck, Germany) in 0.1 mol L⁻¹ nitric acid, and then diluting to 50.0 mL. A stock standard solution for Fe³⁺ was prepared (at the same concentration of Fe²⁺) by dissolving 0.4321 g of ammonium ferric sulfate dodecahydrate (Fluka, Switzerland) in 50.0 mL of DI water. Standard solutions were stored in plastic bottles, and the concentrations were determined by EDTA titration.

Sample solutions
Water samples were collected from natural sources including various pools within Thammasat University and a paddy field in Pathum Thani Province. Samples were filtered with 0.20 μm nylon filters (National Scientific, Rockwood, TN) and kept in polyethylene bottles at 4°C. Samples were analyzed within one hour after collection.

Results and Discussion
Microfluidic device configuration
As described in the Experimental section, a single PMMA substrate (30 mm × 30 mm × 5 mm) was used to fabricate a pattern of microchannels (microreactors) having a total capacity of 2.7 mL. To ensure sufficient sample-reactant mixing and reaction time, the length of the microchannel was maximized by using a zigzagging profile, beginning at the substrate corner and extending along the diagonal direction. Channels 250-μm wide, 100-μm depth, and 27.6-cm long were fabricated on both sides of the substrate. A flow cell for monitoring reactions conducted in the device was included in the design. This flow cell had a 1 mm i.d. and a depth of 4 mm, creating a total capacity of 3.1 mL. Microchannels intersected with each other at the corner of each side, and the two optical detectors were aligned in appropriate positions for monitoring the colorimetric signal.

Optimization of the system
The optimal flow rate for each reagent- or carrier solution-delivering syringe was determined by performing experiments in the range of 10 – 50 μL min⁻¹. The optimum flow rate was found to be 30 μL min⁻¹.

Likewise, the optimal concentration for colorimetric reagents (Phen and KSCN) was determined by conducing analyses of 5 mg L⁻¹ Fe²⁺ and Fe³⁺ using the previously determined optimal flow rate. For Fe²⁺ analysis, the working concentrations of KSCN were varied from 0.01 to 0.1 mol L⁻¹. As shown in Fig. 2 (line A), the highest signal for Fe²⁺ analysis was obtained when using 0.06 mol L⁻¹ of KSCN. Similarly, for the determination of Fe³⁺, various concentrations of Phen between 1.0 × 10⁻³ and 2.0 × 10⁻² mol L⁻¹ were tested. As indicated in Fig. 2 (line B), it was found that the best signal for Fe²⁺ was obtained when using 5.0 × 10⁻³ mol L⁻¹ of Phen. These colorimetric reagent concentrations were used in all subsequent Fe²⁺ and Fe³⁺ analyses.
Tolerance for the speciation of Fe^{2+} and Fe^{3+}. The results of figures of merit, including the linearity, limit of detection 7.2 mL h^{-1}, and each reagent was consumed at a rate of approximately 1.8 mL h^{-1}.

For these calculations, LODs were expressed as th signal-to-noise ratio (3\sigma / S_i). Representative LOD signals are collected for samples containing 0.1 and 0.5 mg L^{-1} of Fe^{2+} and Fe^{3+}, respectively, corresponding to 3 S/N.

Analytical figures of merit

The system was characterized by measuring the analytical figures of merit, including the linearity, limit of detection (LOD), reproducibility, repeatability, recovery, and interference tolerance for the speciation of Fe^{2+} and Fe^{3+}. The results of linearity, precision, and LOD analyses are presented in Table 1. The linear range of this method was evaluated by the analysis of 0.1 – 20 and 1 – 40 mg L^{-1} concentration ranges for Fe^{2+} and Fe^{3+}, respectively. Calibration curves were generated by plotting the signal (mV) versus concentration (mg L^{-1}), and are shown in Fig. 3(a). The correlation coefficients for Fe^{2+} and Fe^{3+} were calculated to be greater than 0.99, showing good linearity over the tested concentration ranges. Additionally, Table 1 shows the results from injection throughput experiments. For an injection throughput rate of 180 h^{-1}, the total generated waste was 7.2 mL h^{-1}, and each reagent was consumed at a rate of approximately 1.8 mL h^{-1}.

When using optimized reagent concentrations and flow rates, the LODs were calculated to be 0.1 and 0.5 mg L^{-1} for Fe^{2+} and Fe^{3+}, respectively. For these calculations, LODs were expressed as the concentration of Fe^{2+} or Fe^{3+} corresponding to 3-times the signal-to-noise ratio (3 S/N). Representative LOD signals are presented in Fig. 3(b). Assays for testing the reproducibility were carried out by injecting ten aliquots of mixed standards containing 1.0 mg L^{-1} of Fe^{2+} and 5.0 mg L^{-1} of Fe^{3+}. The results from these experiments revealed that the relative standard deviations (RSD) for Fe^{2+} and Fe^{3+} analyses were 6.1 and 6.7%, respectively. The repeatability of this method was assessed using 10 replicate injections of the same mixture. Results from these experiments showed that the RSD values for Fe^{2+} and Fe^{3+} were 5.2 and 6.3%, respectively.

Recovery studies were carried out by spiking water samples with known concentrations of Fe^{2+} and Fe^{3+} (1, 2, 5, 10, 15, and 20 mg L^{-1}), followed by subsequent analysis. The results from these experiments, summarized in Table 2, show that the recovery for Fe^{2+} was in the range of 93.5 – 99.0%, while the recovery of Fe^{3+} was approximately 98.4 – 104.2%.

The intended purpose of this device is for the analysis of Fe^{2+} and Fe^{3+} in natural water using colorimetric detection. However, natural water often contains coexisting heavy metal ions at low concentrations, which can possibly interfere within iron analysis. Thus, experiments that determined the assay tolerance limits of the potential interfering ions were performed. In these experiments, the error produced by interfering ions should ideally not exceed 5%. Specifically, the effects of Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, and Mn^{2+} on Fe^{2+} analysis were examined. For this, a 10 mg L^{-1} solution of Fe^{2+} was mixed with interfering ions at concentrations of 5, 10, 20, 30, and 40 mg L^{-1}, and then analyzed using the microdevice. For Fe^{3+} analysis, the tolerance limits were 20 mg L^{-1} for Fe^{3+} and 10 mg L^{-1} for Al^{3+}, Zn^{2+}, Cu^{2+}, and Mn^{2+}. Following a similar procedure, the tolerance limits of interfering ions for Fe^{2+} analysis were determined to be 30, 20, 10, 20, and 20 mg L^{-1} for Fe^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}, and Mn^{2+}, respectively.

**Analysis of natural water samples**

The DSMs was used to determine Fe^{2+} and Fe^{3+} concentrations in natural water samples. Unfortunately, Fe^{2+} in natural water was not detectable with this system. Thus, a standard addition method was used to analyze Fe^{2+}. As summarized in Table 3, the amount of Fe^{2+} in each sample was found to be no more than 50 μg L^{-1}, and Fe^{3+} was detected to be in the range of 0.7 – 1.6 mg L^{-1}. Complementarily, the Fe^{2+} and Fe^{3+} in samples were also analyzed by batch colorimetry, and the total Fe was determined by ICP spectroscopy. The amounts of Fe^{2+} and Fe^{3+} quantified with the developed microdevice were not significantly different from the results obtained using batch colorimetry, yielding t-statistics of 1.50 and 1.05, respectively, at a 95% confidence level. Moreover, the amount of total iron measured with the developed device was not significantly different from what was found using ICP spectroscopy (with a 95% confidence limit, t-statistic was 1.0 and t-critical with four degrees of freedom was 2.78).

### Table 1 Analytical specifications of the microdevice when used for the analysis of Fe^{2+} and Fe^{3+}

| Analytical feature | Fe^{2+} | Fe^{3+} |
|-------------------|---------|---------|
| 1) Linearity       | Range/mg L^{-1} | 0.10 – 20 | 1.0 – 40 |
|                    | Slope ± S_mV, mV mg^{-1} | 0.07205 ± 0.00090 | 0.03901 ± 0.000075 |
|                    | Intercept ± S_i mV | 0.02365 ± 0.00344 | 0.04665 ± 0.000575 |
|                    | R² | 0.9988 | 0.9974 |
| 2) Precision (% RSD, N = 10) | | | |
| Repeatability      | 5.2 | 6.3 |
| Reproducibility    | 6.1 | 6.7 |
| 3) Limit of detection (3 S/N/mg L^{-1}) | 0.1 | 0.5 |
| 4) Injection throughput/h^{-1} | 180 | 180 |

The limit of detection was calculated to be greater than 0.99, showing good linearity over a 10 mg L^{-1} solution of Fe^{2+} and Fe^{3+}, respectively. The repeatability of this method was assessed by injecting ten aliquots of mixed standards containing 1.0 mg L^{-1} of Fe^{2+} and 5.0 mg L^{-1} of Fe^{3+}. The results from these experiments revealed that the relative standard deviations (RSD) for Fe^{2+} and Fe^{3+} analyses were 6.1 and 6.7%, respectively. The repeatability of this method was assessed by injecting ten replicates of the same mixture. Results from these experiments showed that the RSD values for Fe^{2+} and Fe^{3+} were 5.2 and 6.3%, respectively.

Recovery studies were carried out by spiking water samples with known concentrations of Fe^{2+} and Fe^{3+} (1, 2, 5, 10, 15, and 20 mg L^{-1}), followed by subsequent analysis. The results from these experiments, summarized in Table 2, show that the recovery for Fe^{2+} was in the range of 93.5 – 99.0%, while the recovery of Fe^{3+} was approximately 98.4 – 104.2%.

### Table 2 Percent recoveries from samples spiked with Fe^{2+} and Fe^{3+}

| No. | Added/ Found/ mg L^{-1} | Recoveries, % | Added/ Found/ mg L^{-1} | Recoveries, % |
|-----|------------------------|---------------|------------------------|---------------|
| 1   | 1.0                    | 0.99          | 99.0                   | 1.1           | 1.02          | 102.5       |
| 2   | 2.0                    | 1.87          | 93.5                   | 2.2           | 2.05          | 104.2       |
| 3   | 5.0                    | 4.88          | 97.6                   | 5.0           | 5.21          | 99.1        |
| 4   | 10.0                   | 9.70          | 97.0                   | 10.0          | 9.91          | 103.1       |
| 5   | 15.0                   | 14.65         | 97.7                   | 15.0          | 15.47         | 98.4        |
| 6   | 20.0                   | 19.05         | 95.3                   | 20.0          | 19.67         | 102.5       |

A. S_m and S_i are standard deviation of slope and intercept, respectively.

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Fig. 3 Data from studies used to determine the linear range and LOD for Fe^{2+} and Fe^{3+} analyses. (a) Calibration curves collected for Fe^{2+} and Fe^{3+} using the developed microfluidic system. (b) Signal collected for samples containing 0.1 and 0.5 mg L^{-1} of Fe^{2+} and Fe^{3+}, respectively, corresponding to 3 S/N.

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Analytical feature Fe^{2+} Fe^{3+}

| No. | Added/ Found/ mg L^{-1} | Recoveries, % | Added/ Found/ mg L^{-1} | Recoveries, % |
|-----|------------------------|---------------|------------------------|---------------|
| 1   | 1.0                    | 0.99          | 99.0                   | 1.1           | 1.02          | 102.5       |
| 2   | 2.0                    | 1.87          | 93.5                   | 2.2           | 2.05          | 104.2       |
| 3   | 5.0                    | 4.88          | 97.6                   | 5.0           | 5.21          | 99.1        |
| 4   | 10.0                   | 9.70          | 97.0                   | 10.0          | 9.91          | 103.1       |
| 5   | 15.0                   | 14.65         | 97.7                   | 15.0          | 15.47         | 98.4        |
| 6   | 20.0                   | 19.05         | 95.3                   | 20.0          | 19.67         | 102.5       |
Comparison with other flow analysis methods

The DSMs has been compared to similar flow-analysis devices in terms of the configuration and analytical features. The zigzagging reactor channels in the presented design, each with a length of 27.6 cm, permitted a sufficient fluid mixing and reaction time for colorimetric detection. A previous report by Kruanetr et al. described a T-shaped reactor 2 cm in length that was ideal for the analysis of Fe using a fast-reacting Nitriso-R salt when coupled to a fiber optic spectrometer. Although the reaction channel length was shorter, the reported sample throughput was only 40 h⁻¹. Using the microdevice reported here, a sample throughput of 180 h⁻¹ was achieved. This sample throughput is similar to that described in the work of Koronkiewicz and Kalinowski, in which a direct injection detector was integrated with a multi-pumping flow system for total Fe analysis. Moreover, the method proposed here offers higher sample throughput when compared to another system for Fe speciation which uses a multi-syringe flow system and a chelating disc for the oxidation of Fe²⁺ to Fe³⁺ (sample throughput of 5–10 injections h⁻¹).

The LODs obtained with the device presented here are higher than those reported from other systems. However, this system could be integrated with a preconcentration device such as a solid-phase extraction cartridge or column. The major advantage in using the system proposed here is the capability to perform simultaneous multiple analyses. Additionally, a low rate of reagent consumption and waste generation yields a greener analytical system.

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Conclusions

In this work, a DSMs capable of multi-analyte quantification is reported. This device consists of microchannel networks fabricated onto both sides of a single substrate and an integrated LED-LDR sensor built in-house. The device achieved low reagent consumption and waste generation rates, and thus helping to realize the objectives of GAC. This miniaturized system is capable of being further integrated into a portable apparatus, and can also be made fully automated for real-time analysis at such on-site locations as rivers and water desalination and treatment plants. In this work, the device was used to analyze Fe²⁺ and Fe³⁺ present in natural water sources. However, it can be used for the analysis of other ions as well. Ongoing work involving this project includes using a similar concept to develop a simple, miniaturized device for the monitoring of additional parameters.

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