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# Miniaturization of spectrophotometry based on micro flow analysis using norfloxacin as less-toxic reagent for iron determination

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## HIGHLIGHTS

- We assemble an environmental friendly, simple, rapid μFA for iron assay.
- We use a norfloxacin as less toxic reagent for iron determination.
- It can reduce chemical/reagent consumption with low chemical waste release.
- This method has wide linear range, high selectivity and high precision.
- The procedure has been successfully applied for iron analysis in water sample.

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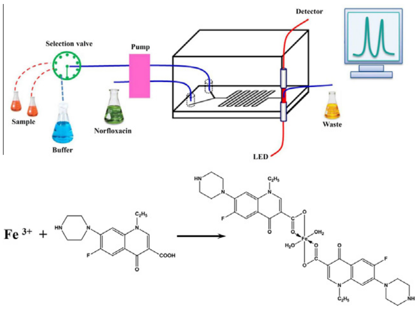
## GRAPHICAL ABSTRACT



## ABSTRACT

A micro flow analysis (μFA) system has been designed and fabricated for determination of total iron. The system consists of a microchannels fabricated by etching the polymethyl methacrylate (PMMA) by using laser ablation techniques and a sealed polydimethylsiloxane (PDMS) as top plate. The PMMA micro-flow was topped with a home-made polydimethylsiloxane (PDMS) micro-flow through cell, which was integrated with light emitting diode (LED) as light source and a USB 2000 spectrometer as detector. The proposed μFA system was applied to determination of Fe(III) using norfloxacin as a less-toxic complexing agent in an acetate buffer solution pH 4.0, resulting in a yellow colored complex which gave the maximum absorption at 430 nm. Under the optimum conditions, a linear calibration graph was obtained in the concentration range of 0.20–5.00 mg $L^{-1}$. The limit of detection (LOD, defined as $3\sigma$) and limit of quantification (LOQ, defined as $10\sigma$) were 0.12 and 0.45 mg $L^{-1}$, respectively. The relative standard deviation (R.S.D.) for repeatability and reproducibility were less than 1.50% and 1.24% ($n = 11$) for 0.2 mg $L^{-1}$ and 1.0 mg $L^{-1}$ Fe(III), respectively. The proposed method was successfully applied to the determination of total iron in water samples, validated by the FAAS standard method after digestion by $HNO_3$ and $H_2O_2$.

## 1. Introduction

Iron is the fourth most abundant element in the earth's crust and is one of the most important elements in geochemical, environmental and biological systems [1]. In nature, iron combined

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with other elements forming iron ore, such as oxide ores and mineral limonite. Generally, iron in water comes from dissolution of iron compound in soil, leaching into the ground water, where it distributes into wells and aquifers that used to supply drinking water [2]. In ground water, iron concentration ranges typically between 0.5 and 10.0 mg $L^{-1}$, but concentrations up to 50 mg $L^{-1}$ may locally be found [3,4]. Iron concentration in drinking water is normally less than 0.3 mg $L^{-1}$ but may be higher when various iron salts are used as coagulant in water-treatment plants, and when cast iron, steel and galvanized iron pipes are used for water distribution. In river waters, the median iron concentration has been reported to be 0.7 mg $L^{-1}$ [4]. It is well known that iron deficiency is the most common cause of anaemia. On the other hand, too much iron can cause a several health problems. High levels of iron are associated with an increased risk for cancer, heart disease, and other illnesses such as endocrine problems, arthritis, diabetes, and liver disease [5]. Accordingly, accurate determination of iron is very important to this regard.

Currently, a number of analytical techniques have been developed for iron determination, including atomic absorption spectrophotometry [6], inductively coupled plasma mass spectrometry [7], liquid chromatography [8,9], electrochemistry [10,11] and spectrofluorimetry [12,13] and flow-based techniques [14–18]. The latter is one of the most efficient method that is frequently used for iron determination, particularly in the form of Fe(III) assays. For example, Ruengsitagoon [14] employed flow injection analysis (FIA) along with chlortetracycline for determination of Fe(III). Kawashima et al. [15] described the FIA method that is based on the catalytic effect of Fe(III) on the oxidation of 3,3′,5,5′-tetramethylbenzidine with hydrogen peroxide. Although they are superior to the batch-wise methods in that they provide relatively high sample throughput, low reagents and sample consumptions, low analysis time and cost effectiveness. Some of which typically uses high reagent consumptions and makes a large amount of waste especially dealing with expensive chemicals, hazardous reagents, or online/remote site applications. Thus, the FIA technique is a relatively expensive method by comparison with the second generation termed sequential injection analysis (SIA).

Sequential injection analysis (SIA) is considered as a second concept flow-based analysis. The basic principles of SIA are similar to those of FIA, namely controlled partial dispersion and reproducible sample handling. Additionally, it is fully automated system to make it fast and efficient that is important to many routine tasks. Much effort has been made recently to develop the SIA system for Fe(III) determination based on various complexing agents. Viollier et al. [16] modified the SIA system for determining the Fe(II) and Fe(III) by using ferrozine as complexing agent. Galhardo et al. [17] applied the SIA using 1,10-phenantroline and reducing agent as a tool for *in situ* monitoring of Fe(II) and Fe(III). Kruanetr et al. [18] presented the SIA method using deferiprone for iron determination. However, these techniques are infrequently used in field work due to instrument size and a non-portable nature. The development of these flow-based systems has brought a new dimension to analytical chemistry, allowing the measurements to be carried out faster and with minimum intervention of the analyst. Although there are many reliable flow procedures for routine analysis, most of them cannot be considered environmentally friendly, because they produce chemical wastes that can be toxic and need to be suitably managed. Despite this, the potentiality to develop greener analytical procedures is inherent to advanced flow-based system methodologies [19].

Microflow analysis has been growing in important for a number of years, and is now accepted as an alternative to some conventional analytical approaches. Moreover, micro flow analysis is one of analytical techniques that provide rapidity, high sensitivity and low waste produced [20]. It involves the miniaturization of all functions in chemical analysis, including sampling, removal of interferences, small amount of chemical consumption, and small size of mixing reactor and/or reaction chamber [21]. The entire chemical measurement device could be miniaturized onto a few square centimeters [19].

Applications of microflow injection analysis (μFA) in Fe(III) determination based on spectrophotometric detectors are required chemical complexing agents. For example, Kruanetr et al. [22] used μFA to determine the amount of Fe(III) by using nitroso-R-salt. Besides, Alsuhaimi et al. [23] developed microfluidic device for analysis the Fe(II) and Fe(III) by using KSCN and 1,10-phenantroline, respectively. Some other reagents are also used including quercetin [24], morin [24], 7-iodo-8-hydroxyquinoline-5-sulphonic acid [25], 4-aminoantipyrene [26], 2-hydroxyl-5-methyl benzophenone oxime [27], 3-hydroxyl-3-phenyl-l-m-chlorophenyl triazene [28], thioglycolic acid [29] and diformyl hydrazine [30]. However, the use of those reagents is still limited as they are toxic to humans. Thus, the developing of a non-toxic reagent which is sensitive, less toxic chemical in waste production, cost effective and human friendly is still needed.

Norfloxacin or 1-ethyl-6-fluoro-4-oxo-7-piperazin-1-yl-1Hquinoline-3-carboxylic acid is a synthetic chemotherapeutic antibacterial agent occasionally used to treat common as well as complicated urinary tract infections [31]. Norfloxacin (Fig. 1a) has been determined spectrophotometrically through complexation with Fe(III) and subsequent measurement of the yellow 1:2 complex (Fig. 1b) and this complex is stable with the maximum absorption wavelength at 377 nm in ammonium sulfate–sulfuric acid media which was adopted from the reported batchwise method [32].

In this work, micro flow analysis is proposed for minimizing the use of sample and chemical reagents and diminutive waste generation for Fe(III) determination by using norfloxacin as a less-toxic reagent. The experimental conditions were carefully optimized and a detailed assessment of the possible interferences was carried out. The results of applying this method to the measurement of iron in water samples are presented and showed to be in good agreement with those obtained by previously utilized methods.

## 2. Experimental

### 2.1. Chemical and reagents

All chemicals were of analytical reagent grade and were used without further purifications unless otherwise specified. All solutions were prepared with deionized water.

Standard stock solution of Fe(III) 10.00 mg $L^{-1}$ was prepared from a standard iron(III) solution (AAS standard, 1000 mg $L^{-1}$ Merck, Germany). Working standard solutions were prepared by appropriate dilution of this stock standard solution.

Norfloxacin was purchased from Fluka. Its stock reagent solution (0.01 mol $L^{-1}$) was prepared by dissolving 0.3193 g of this reagent in water and diluting to 100 mL.

Acetate buffer solution (0.1 mol $L^{-1}$ at pH 4.0) was prepared by dissolving 1.3608 g of sodium acetate (Carlo Erba, Italy) in 50.00 mL of deionized distilled water in a 100 mL volumetric flask and adjusted pH to 4.0 by using a glacial acetic acid (Merck, Germany) and diluted with water in a 100 mL volumetric flask.

### 2.2. Apparatus

The ten-port selection valves with zero dead volume (VICI, Valco Instruments) introduction of standard or sample and buffer solutions into μFA system and equipped with a Micro peristaltic pump (ISMATEC, Switzerland) for controlling suitable flow rate in this system.