

A new merging-zone flow injection system for the quantification of ferrous and ferric ions in aqueous solution and sludge of wastewater

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Abstract: A simple and fast throughput flow injection (FI) system with a merging-zone technique was designed to determine ferrous and ferric in an aqueous solution. The method is based on the direct reaction of ferrous with a Bathophenanthroline reagent (Bphen) in acidic media. The forming red complex absorbs light at 533 nm. All conditions of the flow injection system were investigated. The analytical curve of ferrous was linear in the range of 0.07 to 4 mg/L with an r^2 value of 0.9968. The detection and quantification limits were 0.02 and 0.04 mg/L, respectively. The molar absorptivity and Sandell's sensitivity were 4.0577×10^6 L/mol cm and 25×10^{-5} $\mu\text{g}/\text{cm}^2$, respectively. The homemade valve was low-cost with high repeatability ($n = 7$) at an RSD of 1.26 % and zero dead volume. The values of the dispersion coefficient were 2.318, 2.022, and 1.636 for the concentrations of 0.2, 1, and 3 mg/L, respectively. The analysis throughput of the designed flow injection unit was 57 sample per hour.

Key words: merging-zone, ferrous and ferric, bathophenanthroline, dead volume, homemade valve

1. Introduction

Iron is one of the main trace elements in many industrial, biological, electroplating processes, nanotechnology, sewage sludge, and organic fertilizers.¹⁻³ Ferrous is directly reacted with 4,7-Diphenyl-1,10-phenanthroline (Bphen) to form a red complex that absorbs at 533 nm.^{4,5} The merging-zone FI technique requires a low amount of chemicals.^{6,7} Consequently, a handmade valve can be utilized to estimate ferrous with Bphen by a merging-zone FI system.

Ferric is determined in drugs by complexation

titration at reacting with EDTA.⁸ Ferrous is also estimated by the redox titration using potassium permanganate as an oxidizing agent.⁹ Similarly, ferrous was determined by redox titration using potassium dichromate and diphenylamine indicator.¹⁰ However, this method produces large chemical waste volumes, requests an indicator, and has higher Human error.¹¹ Ferric was estimated using the gravimetric method by precipitating it with ammonium hydroxide.¹² Nevertheless, it requests time consumption and analysis of a single element.¹¹ Ferrous was determined spectrophotometrically using methyl thymol blue.¹³

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Total iron in environmental samples was estimated by spectrophotometry with a Nitroso R salt reagent.¹⁴ Ferrous at nano-scale concentrations in seawater was also determined spectrophotometrically using a Ferrozine reagent.¹⁵ However, the UV-VIS spectrometer requires clearing the region of outside light and electronic noise and needs time for preparing to use.¹¹ Ferrous in ethanol was estimated by potentiometric using a glass electrode coated with a PAN reagent which is complexing with ferric.¹⁶ Ferric is determined in trace amounts in environmental samples by potentiometric using a selective electrode based on benzo-18-crown-b.¹⁷ Nonetheless, potentiometric has low accuracy, limited bandwidth, needs strength for contact, and freshly prepared electrolyte.¹¹

Ferrous and ferric determine by different FI methods. It has been estimated at trace concentration in drinking water by a stop-flow system using phenanthroline.¹⁸ In addition, it estimate by the continuous FI method with the same reagent in the Shatt Al-Arab waters.¹⁹ Also, iron was calculated in coastal waters by reverse FI technique, as the iron sample was utilized as a carrier solution.²⁰ Iron was estimated by sequential injection in pharmaceutical with phenanthroline reagent at a sampling of 40 per hour.²¹

This study describes a new merging-zone technique to determine ferrous by FI. This method is high throughput, simple, and high precision approach for determining ferrous and ferric in an aqueous solution and wastewater sludge using a low-cost handmade valve. Ferrous is directly reacted with a specific Bphen reagent in acidic media to form a red complex that absorbs at 533 nm.

2. Experimental

2.1. Materials

4,7-Diphenyl-1,10-phenanthroline (Bphen) (Merck), Ferrous sulfate heptahydrate (BDH), Ferric nitrate nonahydrate (Merck), Hydroxylamine hydrochloride (BDH), Nitric acid (BDH), hydrochloric acid (Chem-Lab), sodium hydroxide (Merck), absolute ethanol (Chem-Lab), and Glacial acetic acid (BDH) were used. The reagents and chemicals used were of analytical

grade. The water used was distilled and deionized.

2.2. Apparatus

The carrier solution was propelled using pump with a 4-channel Peristaltic from Ismatec (Germany). The solution of sample and reagent were injected using a manual FI valve composed of plastic, acrylic, and four three-way dispenser. A single-beam APEL, PD-303 (Japan) UV spectrophotometric was utilized to obtain spectrometric measurements via a FI system. To acquire data as a peak height, the spectrophotometer was coupled to the Kompensograph recorder C1032 Siemens (Germany). The flow cell (1 cm optical path) with a volume aptitude of 450 μ L and two vents for outputting and inputting the carrier solution was obtained from Helmma (UK). The pH was measured using a Philips Pw 9421 (Germany) pH meter. The maximum wavelength was established utilizing the double-beam spectrophotometer Shimadzu UV-1700 (Japan).

2.3. Solutions

A stock solution of ferrous 100 mg/L was prepared in distilled water (DW) from ferric sulfate heptahydrate by the dissolution of 0.0248 g in a small amount of DW, then 100 μ L of concentrated hydrochloric acid was added, posteriorly the volume was completed with DW to 50 mL. Working solutions of ferrous were prepared by dilution with DW simultaneously.²² Ferric stock solution of 100 mg/L was prepared from ferric nitrate nonahydrate by the dissolution of 0.0361 g in a few amount of DW, then 100 μ L of concentrated hydrochloric acid was added, then the volume was completed with DW to 50 mL. Working solutions were prepared by dilution with DW freshly.²² Bphen prepares by dissolving in ethanol and it is also prepared by dissolving in acetic acid.²³ Bphen was prepared at 300 mg/L and in a volume of 50 mL (a solution of 4 % absolute ethanol and 2 % acetic acid concentrated) daily. 0.0150 g of the Bphen reagent was dissolved in 2 mL of ethanol alcohol, then 1 mL of concentrated acetic acid was added, and the volume was completed by DW to 50 mL. Dilute solutions of the Bphen reagent were prepared by

dilution with DW simultaneously. A solution of Hydroxylamine hydrochloride was prepared at a concentration of 1 % by DW (weight-to-volume ratio). The carrier solution is hydrochloric acid modified to a pH of 5.

2.4. Procedure for sludge²⁴

The sludge was taken from the sedimentation basins of the Al-Maamera wastewater treatment station, which is located 3 km south of Babylon city in Iraq. The sludge possessed was dried in an oven at 105 °C for four hours, then the dried sludge was crushed using a ceramic mortar and sifted to 300 µm. The concentration of ferrous and ferric in the sludge was estimated after acid digestion. A 0.5000 g of dried sludge with a particle size of 300 µm was weighed and was digested for two hours at 90 °C using 4 mL of concentrated nitric acid and 12 mL of concentrated hydrochloric acid. After cooling, 100 mL of DW was added, then the supernatant was separated by centrifugation.

2.5. Flow injection system analysis module

A new FI system with a merging-zone technique that depends on spectrophotometric detection for determining Fe(II) in an aqueous solution and sludge of wastewater as a simple and fast system is shown in Fig. 1, where: P is the peristaltic pump, C is the carrier solution (HCl at pH of 5), V is the homemade injector valve (with two loops), S is the ferrous loop, R is the Bphen reagent loop, W1 is the injection valve waste (reagent and sample), RC is the reaction coil, D is the UV-VIS spectrophotometer 533 nm, K is the Kompensograph at 0.5 volts, and W2 is the system waste.

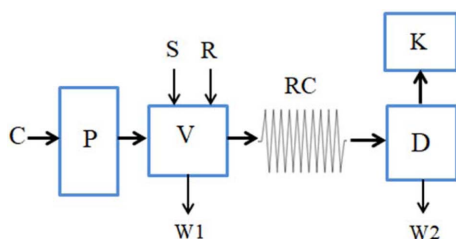


Fig. 1. Graphical diagram of the FI system for determining Fe(II).

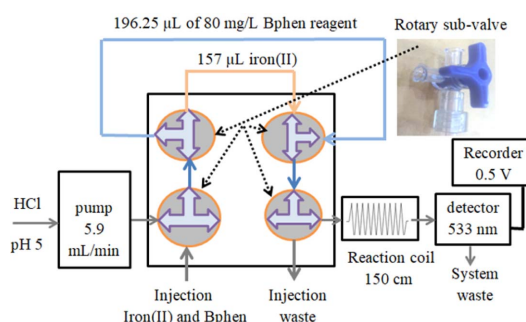


Fig. 2. Graphical diagram of the valve work.

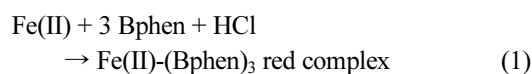
2.6. Recommended procedure

The diagram for the mechanical operation process of the homemade valve shows in Fig. 2. The first step involved the propel of hydrochloric acid that was adjusted at pH 5 as the carrier to all the unit parts by a pump at a flow rate of 5.9 mL/min. HCL represents the blank solution and provides the acidic media for the reaction between Bphen and ferrous. The second and third steps encompass stopping the pumping HCl and injecting 196.25 µL of 80 mg/L Bphen in the particular loop (represented by the blue line in Fig. 2) and injecting 157 µL of the Fe(II) sample in the specific loop (represented by the brown line in Fig. 2). Then HCl carries the ferrous and Bphen solutions from loops to the reaction coil of 150 cm. Ferrous reacts with Bphen in acidic media to form a red complex that absorbs light at 533 nm. The alteration in response height of the Kompensograph recorder was proportionate to the Fe(II) concentration/ reference carrier (HCl).

3. Results and Discussion

3.1. Method principle

The ferrous determination method that is used in this article is based on a direct reaction between ferrous and Bphen in the acidic media of HCl. Fe(II)-Bphen complex is red and absorbs light at 533 nm.⁴ The combination ratio is Fe(II) 1:3 Bphen,⁵ as shown in Fig. 3. The reaction which occurs is as follows:



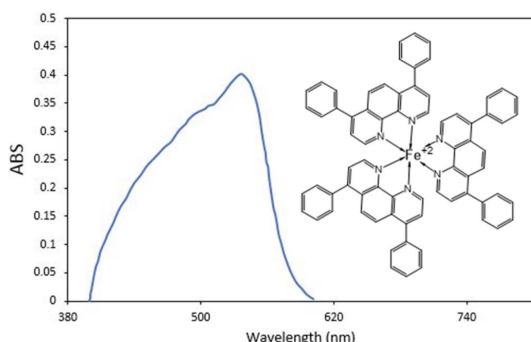


Fig. 3. Absorption spectra of Fe(II)-Bphen complex. Wavelength 533 nm at Fe(II) 10 mg/L, Bphen 300 mg/L, and pH 5

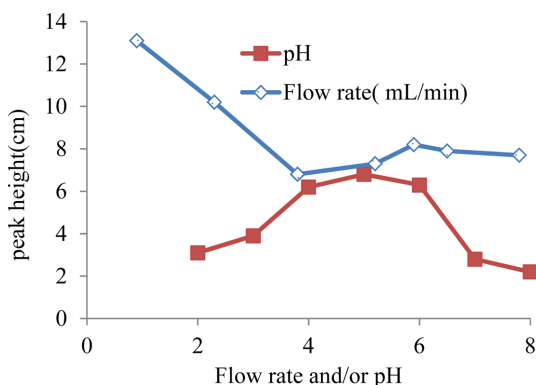


Fig. 4. The effect of flow rate and pH.

3.2. Effect of pH

The pH effect was studied within a range of 2-9. The conditions involved a flow rate of 3.8 mL/min, 157.00 μL of 100 mg/L Bphen, a reaction coil of 200 cm, and 117.75 μL of 3 mg/L Fe(II) sample. As depicted in Fig. 4, the perfect pH was five at a peak height of 5 cm. The result acquired in this study coincide with the outcome of Derman *et al.*,²⁵ and Kok and Wild.²⁶

3.3. Effect of flow rate

The effect of the flow rate of the carrier solution represented by HCl within the range of 0.9-7.8 mL/min was studied. The optimum flow rate was determined under pH of 5. Other reaction conditions were 157.00 μL of 100 mg/L for the Bphen, a reaction coil length of 200 cm, and 117.75 μL of 3 mg/L of the ferrous solution. The results in Fig. 4 show that the low flow rate of 0.9 and 2.3 mL/min give a high

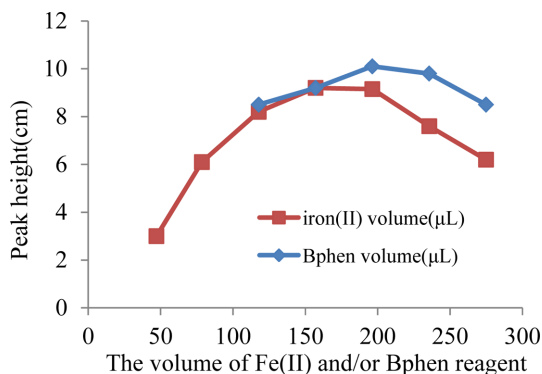


Fig. 5. The effect of ferrous and Bphen volumes.

response at 13.1 and 10.2 cm, respectively, but the shape of the peak is widely and double because the slow rates cause incomplete mixing. After flow rate 3.8, the response increases due to the perfect mixing, and a peak is sharp and reliable while the dispersion effect reduces response at the higher flow rate. Fig. 4 shows that the optimum flow rate is 5.9 mL/min at the response height of 8.2 cm.

3.4. Effect of ferrous volume

The volume of the optimum ferrous solution was determined by changing the lengths of the loop in the homemade injection valve within the range of 47.1-274.75 μL . The flow rate was 5.9 mL/min, and pH was 5, while the other conditions were 157.00 μL of 100 mg/L for the Bphen, the reaction coil length was 200 cm, and the ferrous sample concentration was 3 mg/L. The results show in Fig. 5 that the response first increases with an increase in the volume of ferrous from 47.1 to 157.00 μL , then relative stability is obtained at 196.24 μL whilst the peak height decreases with an increase in an Fe(II) volume because high volumes cause a dilution of ferrous within volume of the reagent and the carrier solution. The optimum volume of ferrous is determined at 157.00 μL with a response of 9.2 cm and a certified sharp peak. Despite the equal response of 157.00 and 196.25 μL volumes were achieved, 157 μL was the volume of choice because green chemistry recommendation tends toward less chemicals consumptions.

3.5. Effect of Bphen volume

The effect of the volume of the Bphen on the response was deliberate within the range 117.75-274.75 μL . In the optimal conditions represented by the pH 5 of the carrier solution, the flow rate of 5.9 mL/min, and the volume of 157.00 μL at the concentration of 3 mg/L for the ferrous sample, while the other conditions were 100 mg/L for the reagent, the reaction coil length of 200 cm, and the results were as in *Fig. 5*. An increase in the response from 8.5 to 10.1 cm was observed at rising the Bphen volume from 117.75 to 196.25 μL . There is a drop in the peak height to reach 8.5 cm, which is attributed to the dilution factor, as the reaction product is dispersed over the large surplus volume of the reagent, so an optimum amount of 196.25 μL was chosen for the Bphen at the highest response of 10.1 cm.

3.6. Effect of reaction coil length

The optimum reaction coil length for the reaction between the Bphen and Fe(II) was estimated. The reaction coils were studied with lengths of 50, 100, 150, 200, 250 and 300 cm under the optimal conditions represented by the pH 5 of the carrier, the flow rate of 5.9 mL/min, 157 μL of 3 mg/L ferrous, and 196.25 μL of 100 mg/L Bphen and the findings were as in *Fig. 6*. The results demonstrate that increasing the coil length from 50 to 150 cm enhances the response because it provides appropriate mixing and gives an ideal dispersion for the reaction materials, whereas the longer length of 200 cm exhibits the

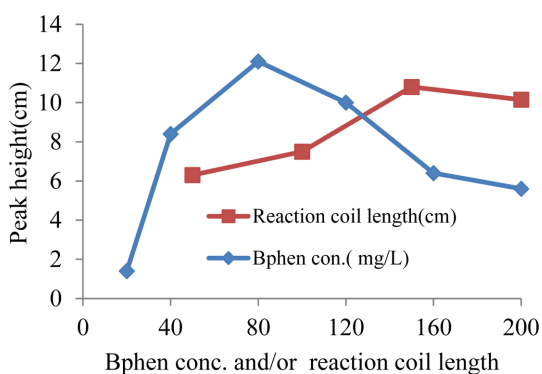


Fig. 6. The effect of Bphen concentration and reaction coil length.

opposite effect as the response declines relatively due to the dispersion factor to 10.15 cm and then the effect appears additional dilution at reaction coils of 250 and 300 cm. At a peak height of 10.8 cm, 150 cm was discovered to be the optimal reaction coil.

3.7. Effect of Bphen reagent concentration

The effect of the Bphen reagent concentration in the range of 20-200 mg/L was studied. The optimum conditions were represented by the pH of 5 for the carrier solution, the flow rate of 5.9 mL/min, 157.00 μL of 3 mg/L ferrous, 196.25 μL of Bphen, and the reaction coil length of 150 cm. The results were as in *Fig. 6*. It was found that increasing the concentration of the reagent from 20 to 80 mg/L increases the response to reach 12.1 cm. It was also noted that high concentrations cause a decrease in response. 80 mg/L was relied on as the best concentration that gives the highest response to the interaction between ferrous and the reagent.

Table 1 shows the optimum conditions needed by the new system developed to determine Fe(II): carrier solution pH, flow rate, Fe(II) and Bphen volume, reaction coil length, and Bphen concentration.

3.8. Calibration curve

The calibration curve was established by doing the measurements under optimal conditions. The graph instituted using series concentrations for Fe(II), as depicted in *Fig. 7*. The calibration curve revealed that Beer's law was linear in the 0.07-4 mg/L range. *Table 2* shows analytical data that can be conclude from the graph.

Table 1. Parameters evaluate to optimize the FI system of Fe(II)

Parameter	Estimate range	Selected value
The pH of the carrier solution	2-9	5
Flow rate (mL/min)	0.9-7.8	5.9
Fe(II) volume (μL)	47.1-196.25	157
Bphen volume (μL)	117.75-274.75	196.25
Reaction coil length (cm)	50-300	150
Bphen concentration(mg/L)	20-200	80

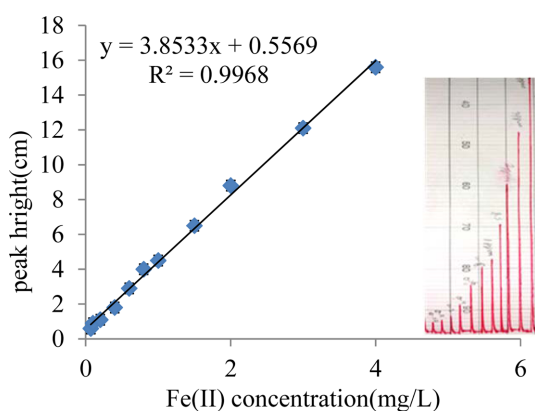


Fig. 7. The calibration curve of Fe(II) determination.

3.9. Repeatability

Repeated injections of the Fe(II) sample at least seven times determined repeatability. The purpose of this investigation was to calculate the measurement precision and the system efficiency of FI. Seven successive injections of the ferrous solution concentrations of 0.2, 1, and 3 mg/L were applied to examine injection repeatability under optimal conditions. RSD values for these concentrations were 2.922, 0.593, and 0.264 %, respectively. The results in Table 2 demonstrate the efficiency and precision of the new FI unit design for determining Fe(II).

3.10. Dispersion Coefficient (D)

Two measurements were achieved under optimal conditions to estimate the dispersion coefficient. Firstly, the reaction components were mixed in a beaker

Table 3. Dispersion Coefficient of FI system

Fe(II)(mg/L)	0.2	1	3
Peak height H^0 (cm)	2.55	9.1	19.8
Peak height H_{max} (cm)	1.1	4.5	12.1
D	2.318	2.022	1.636

outside the FI unit and then measured as a carrier solution. In this case, the response indicates H^0 . The second measurement comprised injecting Fe(II) and Bphen into their designated loops in the valve, with the carrier solution being HCl. In this situation, the response indicates H_{max} . The dispersion coefficient (D) was estimated by dividing H^0 by H_{max} .⁵ Table 3 shows the results.

3.11. Dead Volume

The loading of DW instead of the Fe(II) solution was the first step in determining the dead volume. The second stage was to fill the loop of Bphen with DW. There was no peak appeared in these two stages, but when Fe(II) and Bphen were injected into the definite places, the peak was clear. Under optimal conditions, the carrier solution in both stages was HCl at a pH of 5. As a result of this study, no volume of Fe(II) solution or Bphen solution remained in their loops before the second analysis. Therefore, the valve worked at zero dead volume.

3.12. Comparisons

3.12.1. Sampling Throughput

To inject Fe(II) and Bphen into the loops of the

Table 2. The analytical data of calibration curve and repeatability for determining Fe(II) by FI unit

Analytical data of calibration curve parameter	Value	Repeatability (n=7)			
		Fe(II) (mg/L)	0.2	1	3
Range (mg/L)	0.07-4	Peak height(cm)	1.1	4.5	12.1
Molar absorptivity (L/mole.cm)	4.0577×10^6		1.1	4.5	12.1
Sandal sensitivity ($\mu\text{g}/\text{cm}^2$)	25×10^{-5}		1.15	4.55	12.05
Detection limit (mg/L)	0.02		1.1	4.5	12.05
Quantification limit (mg/L)	0.06		1.05	4.5	12.1
Intercept	0.5569		1.1	4.45	12.1
Slop	3.8533		1.05	4.5	12.15
r^2	0.9968	SD	0.031	0.026	0.031
SD of slope	0.072	RSD	2.922	0.593	0.264
SD of intercept	0.126				

Table 4. Comparison throughput to other techniques for determining Fe(II)

Technique	Reaction time (min)	Sampling (h)	Ref.
Stop-FIA	3	20	18
FIA	33 second	108	19
rFIA	6	10	20
SIA	1.5	40	21
Spectrophotometric	2	30	27
Spectrophotometric	5	12	28
Spectrophotometric	6	10	29
FIA	1.5	40	30
Merging-zone FIA	63 second	57	Current study

homemade valve was taken 25 seconds. The response required 38 seconds for the peak to begin from the baseline to the top height and return to the baseline. Therefore, the FI unit's throughput was 57 samples per hour. Table 4 compares the sampling of the present FI unit to other techniques for determining Fe(II).

3.12.2. volumes, concentrations, and range

When contrasted to other techniques depending on the same reaction between Fe(II) and the Bphen, utilizing the FI unit intended to determine Fe(II) has many advantages. It is significant to demonstrate that this study is distinguished by the use of a low concentration of Bphen of 80 mg/L and a small volume of Bphen at 196.25 μ L. Moreover, the present merging-zone FI system required solely 157 μ L of Fe(II). Table 5 compares the current non-consumptive analytical

system for ferrous determination with other techniques that depend on the same reaction.

3.13. Application

3.13.1. Application in aqueous solution

Ferrous was directly determined with Bphen by the FI unit under optimal conditions. Standard samples prepared at 0.6 and 3 mg/L from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were taken and analyzed. Ferric was determined after reduction, then reaction with Bphen by FI unit. Standard samples prepared at 0.5 and 3 mg/L from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were taken and analyzed after adding the reducing agent hydroxylamine hydrochloride 0.5 mL of 1 % to the ferric solution. The samples containing ferrous and ferric were measured with the FI system by dividing them into two parts, as the first part was injected into the FI system without adding hydroxylamine hydrochloride so that the resulting response is equivalent to ferrous, then the reducing agent with concentration 1 % is added to the second part of the sample and injected into the FI system so that the resulting response is equivalent to total iron. It was applied on two solutions with ferrous and ferric contents of 0.1 and 1.5 mg/L for both ions. Table 6 shows reliable results for the designed FI system based on RSD values of less than 5 % and with a high approval between the prepared concentrations and those obtained from the calibration curve of the system.

3.13.2. Application in wastewater sludge

After digesting the wastewater sludge, the FI system

Table 5. Comparison of the current FI system to other techniques for determining Fe

Technique	Reagent name	Range (mg/L)	Fe volume (μ L)	Reagent volume (μ L)	Reagent con. (mg/L)	Ref.
Spectrophotometric	Phen	1-10	-	2000	500	31
LLE-FAAS	APIBP	1-10	8000	1000	760	32
Spectrophotometric	KSCN	0.5-4.5	-	10000	485000	33
CPE-FAAS	Benzidine	0.25-4	10000	500	10000	34
Spectrophotometric	TGA	0.1-30	5000	1000	61720	35
Spectrophotometric	DMPAN	8-44	-	2500	1000	36
Spectrophotometric	Phen	0.1-5	200	100	2000	37
Spectrophotometric	Bphen	0.7-3	2000	1500	400	26
Spectrophotometric	Bphen	0.008>	1000	15000	332	38
Merging-zone FIA	Bphen	0.07-4	157	196.25	80	Current study

Table 6. Application of ferrous and ferric determination in aqueous solution

Mixing ratio	ion	conc.(mg/L)		E	E%	Recovery
		Taken	Found			
Single	Fe ⁺²	0.6	0.6080	-0.0134	-1.346	98.65
		3	3.0086	-0.0028	-0.287	99.71
Single	Fe ³⁺	0.5	0.4913	0.0174	1.741	101.74
		3	2.9956	0.0015	0.145	100.14
Dual 0.1: 0.1	Fe ⁺²	0.1	0.1020	0.0202	2.016	102.01
	Fe ⁺² + Fe ³⁺	0.2	0.2058	0.0291	2.911	102.91
	Fe ³⁺	0.1	0.1038	0.0380	3.800	103.80
Dual 1.5: 1.5	Fe ⁺²	1.5	1.5294	0.0196	1.957	101.95
	Fe ⁺² + Fe ³⁺	3	2.9956	-0.0015	-0.145	99.85
	Fe ³⁺	1.5	1.4662	-0.0225	-2.253	97.74

Table 7. Application of ferrous and ferric determination in wastewater sludge

Merging-zone flow injection technique				Atomic absorption
Ion	Fe ⁺² (mg/L) n=5	Total Fe (mg/L) n=5	Fe ³⁺ (mg/L) n=5	Total Fe(mg/L) n=5
Con.	4.315	10.621	6.306	10.685
	4.276	10.582	6.306	10.615
	4.237	10.388	6.150	10.607
	4.237	10.388	6.150	10.690
	4.315	10.621	6.306	10.603
Average	4.276	10.520	6.243	10.640
SD	0.0347	0.1089	0.076	0.0389
RSD%	0.813	1.035	1.222	0.366

was applied to determine ferrous, ferric, and total iron. The AA technique was also used in determination for comparison. The results were shown in Table 7.

3.14. F-test and t-test

The new FI unit was successfully applied for determining Fe(II) in wastewater sludge. The acquired results were compared statistically to those attained from the atomic adsorption technique according to t-tests and f-tests at a confidence level of 95 %. Table 8 demonstrates that the calculated values of the t-test and f-test results were lower than the tabulated (critical) values, elucidating that there was no statistically significant difference existed between the FI unit and AA method with the probability(P) values were less than 0.05.³⁹

4. Conclusions

A feasible, fast, simple, and inexpensive system was developed to determine ferrous and ferric by FI using the merging-zone method. The speed and

Table 8. Statistical comparison of f-test and t-test data for FIA unit with AA

t-test					
Technique	Variance (δ^2).10 ⁻³	t calculated	t tabled	P probability	State
A.A	1.9006	2.0685	2.3060	0.0361	Confidence
FIA	14.8426				
f-test					
Technique	Variance (δ^2).10 ⁻³	f = (δ^2/δ^2) calculated	f tabled	P probability	State
A.A	1.9006	0.1280	0.1565	0.0357	Confidence
FIA	14.8426				

simplicity of the unit encompass a direct reaction between Fe(II) and Bphen reagent in acidic media. The designed system had a high sampling throughput when compared with other techniques. The valve included a merging zone that decreasing the volume of the ferrous and Bphen. The valve advantages were low-cost, nearly no maintenance, easy handling, and zero dead volume. The measurements repeatability for this FI unit was precise at low RSD values and when compared to the atomic absorption technique by the t and f test. Therefore, this new system is reliable for determining ferrous and ferric in aqueous solution and wastewater sludge at a broad concentration range.

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