

Spectrophotometric Determination of Iron (II) Levels in Shatt Al-Arab Water by Flow Injection Analysis

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Abstract

Flow Injection Analysis (FIA) was applied to determine Iron (II) concentrations in surface water of the shatt al-arab river, Al-Basrah city, south of Iraq from October 2009 to September 2010. A linear line was obtained over the range 0.25- 1.75 $\mu\text{g/ml}$ of Iron (II) with regression coefficient for seven points is 0.9999. The detection limit was 0.1 $\mu\text{g/ml}$ with %R.S.D for ten replicate analysis of 1.0 $\mu\text{g/ml}$ Iron (II) is 0.095 % . The samples can be analysed at rates exceeding 108 sample per hour .It was noted that Iron (II) concentration ranged 0.20- 1.65 $\mu\text{g/ml}$, whereas the maximum Iron (II) concentration was recorded in winter 2010 and the minimum in spring 2010.

Key Words: Flow Injection Analysis, Iron (II), Spectrophotometry



Introduction

Iron is the second most abundant element in the earth's crust of which accounts elemental iron is rarely found in nature, as iron ions and most commonly found in nature in the form of its oxides. (Sarin et al 2004). Rainwater percolating through soil and rock can dissolve minerals containing iron, ultimately contaminating natural water supply (Wetzel 2001). Iron is found in four different forms, ferric, ferrous, bacterial and organic. Water hardness and acidity largely determine how much iron dissolves in water (Jeffery 1995). Because iron occurs at extremely low concentration in natural water there is a need for more sensitive analytical methods. Several methods and techniques have been reported for determination of iron in different oxidation states (Faizullah et al.1985, Elrod et al.1991.)

Flow injection analysis (FIA) is one of the most popular continuous flow techniques. It is simple and versatile analytical technology for automating wet chemical analysis (Ruzicka and Hansen 2005). FIA system is characterized by very short time and the analytical signals are obtained within seconds and which leads to high sample throughput (Barnett et al.1999).

The aim of the present work was to establish conditions for simple, fast, and accurate flow injection spectrophotometric method for determination of iron (II) in natural water of Shatt Al-Arab river.

Experimental

Study Area and Sampling

A total of 120 samples of natural water of Shatt al-Arab river were collected from nine stations Fig.(1) and Table (1) over a 12 months during the period from October 2009 to September 2010. The water samples were taken from 30cm down the water surface and 1ml of concentrated nitric acid were added to the sample (APHA 1999).

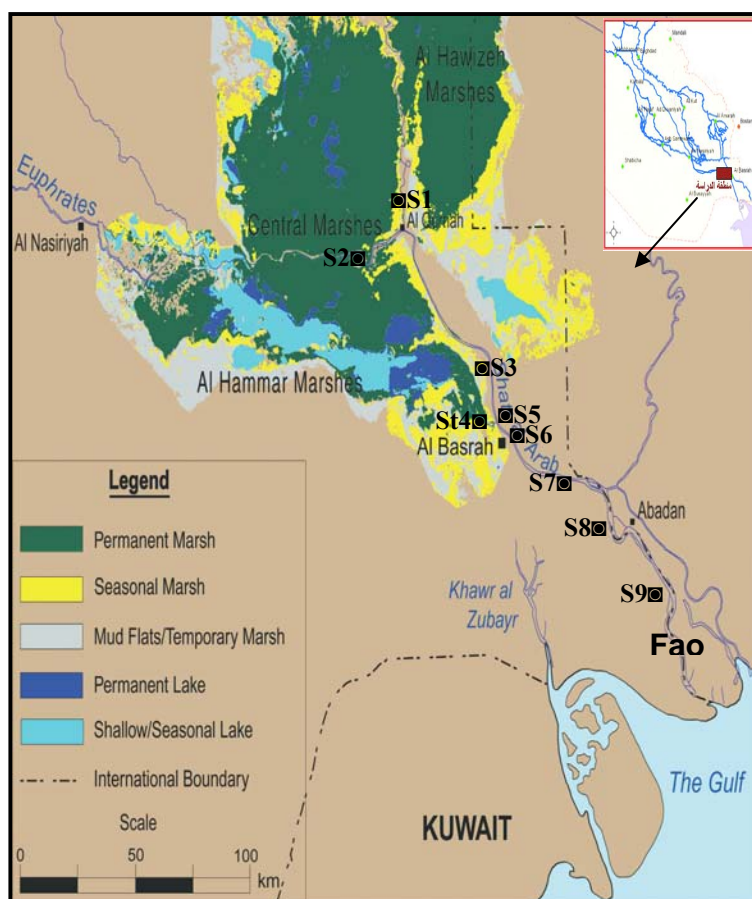


Fig.(1) Study area

Table (1) Study area

Stations	Locations	Latitude	Longitude
St.1	Qurnah (Tigris)	31°00'715"N	47°26'337"E
St.2	Qurnah (Euphrates)	31°00'0.076"N	47°25'0.090"E
St.3	Saad bridge	30°44'155"N	47°41'955"E
St.4	Qarmat Ali	30°34'514"N	47°44'684"E
St.5	Al-Najeebia	30°34'770"N	47°45'974"E
St.6	Ashar	30°31'169"N	47°50'647"E
St.7	Abu Al-khasib	30°27'709"N	48°00'633"E
St.8	Al-Seeba	30°20'210"N	48°15'995"E
St.9	Fao	29°59'359"N	48°27'792"E

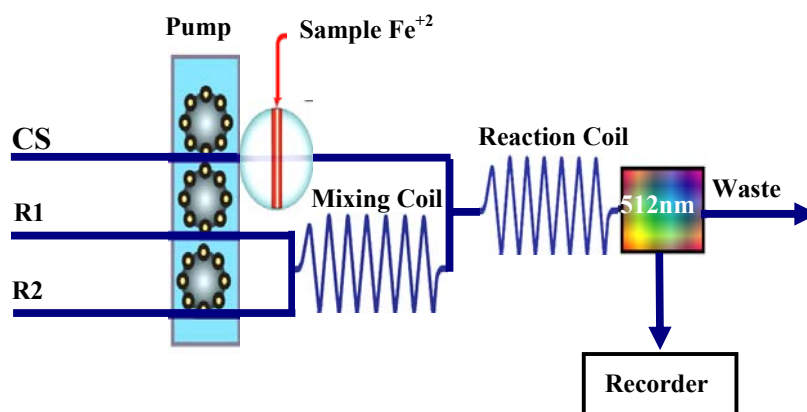
Reagents and Solutions

All Chemicals used were of analytical grade unless otherwise stated and all stock and standard solutions were prepared in deionized distilled water which was used through at this work.

A 1000 $\mu\text{g/ml}$ Iron (II) solution was prepared by dissolving 0.7022g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (BDH) in 100 ml of 0.1M sulphuric acid (GCC). The standards and working solutions were prepared by serial dilution of stock solution. A 1.0% (w/v) 1,10 phenanthroline solution was prepared by Dissolving 1g of 1,10 phenanthroline (BDH) in 100ml of 0.05M of hydrochloric acid solution. This solution were prepared every 4 days and store in plastic bottle (Faizullah and Townshend 1985). Citrate buffers of different pH value were prepared by mixing appropriate volume of 0.1M and 0.1M Sodium citrate to give disred pH value between 3.0 -6.2 (Perrin and Dempsey 1974).

Appratus

A schematic diagram of a home-made flow injection (FIA) system established in marine science center used in this study is shown in Fig.2. A peristaltic pump (Auto-analyzer) with constant speed (16.7 cycle/min) was used for propelling a carrier solution (CS) and a reagent solutions (R1,R2). A six- way valve (RHEODYNE, Catati, California, USA) was used for introducing the standard Iron (II) and sample into the carrier stream. The absorbance was measured with spectrophotometer (shimadzu, UV-150, Japan) equipped with 200 μl flow cell (QS-Hellma) and the Peak heights were recorded with a chart recorder (SIEMENS, Kompensograph). Teflon tube (0.5mm i.d) was used throughout the manifold. All results are the main of six injections of the natural water samples.



CS= 0.15 M Sulfuric acid R1= 1,10 phenanthroline, R2= buffer citrate

Fig.2 Manifold for the determination of Iron (II) in natural water.

Procedures

The flow manifold used for the determination of Fe^{+2} is shown in Figure 2. The carrier stream and reagents were pumped at suitable flow rates. A $90\mu\text{l}$ was injected by rotary injection valve in carrier stream. Different coils length were inserted for mixing the reagents and reaction between the injected sample and the reagents in the flow system. The absorbance of the formed iron (II) complexes were spectrophotometrically with flow cell. The recorded peak heights can be related to the sample concentrations.

Results And Discussion

The following parameters effecting the performance of iron (II) determination in natural water of Shatt al-Arab water with FI system were investigated:

When the manifold in Fig.2 was used, the signal (peak height) of $1.0\mu\text{g ml}^{-1}$ iron (II) increased almost parabolically with increasing injected sample volume Fig 3 between 20-90 μl so,90 was injected in subsequent experimental. The effect of flow rate and total flow rate on peak height of $1.0\mu\text{g ml}^{-1}$ iron (II) in the ranges (0.45-2.0 ml/min) and (1.0-4.0 ml/min) respectively were shown in figures 4 and 5. It was found that 0.8 and 2.0 ml/min flow rate for carrier stream and total flow rate were the best, so they are used in subsequent work.

The influence of reaction and mixing coils length on peak height of ($1.0\mu\text{g ml}^{-1}$) iron (II) in the range (20-90 cm) and (20-120cm) were studied Fig 6 and 7. The results show that 50cm and 40 cm were chosen for reaction and mixing coil length respectively to achieved optimum peak height The greatest peak height was obtained when 0.5% w/v 1,10 phenanthroline, so it was used in subsequent experimental Fig 8.

Fig.9 indicate that peak height increase with increasing of sulphuric acid concentration so,0.15M is the best concentration to be optimized. citrate buffers in (3.25-5) pH ranges for iron (II) determination Fig. 10 show that 4.5 pH value give the best peak height, so it was used throughout this work.

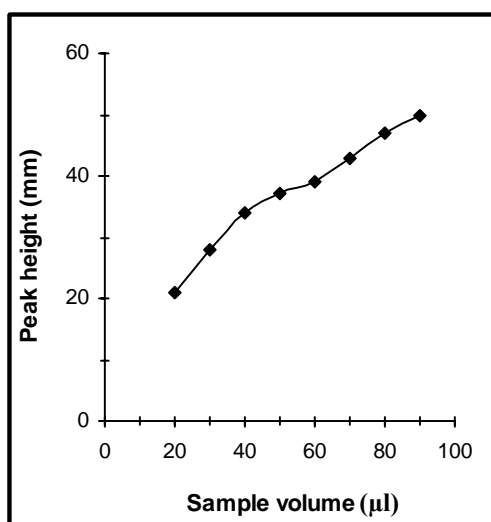


Fig.(3) Effect of sample volume

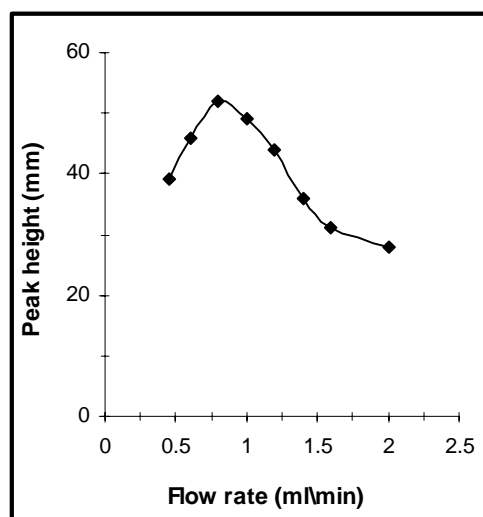


Fig.(4) Effect of Flow rate

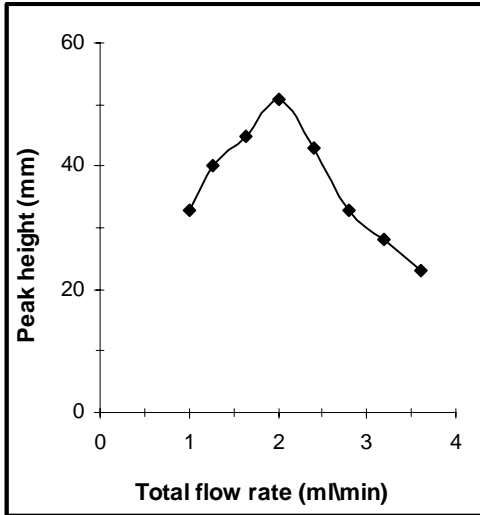


Fig.(5) Effect of Total flow rate

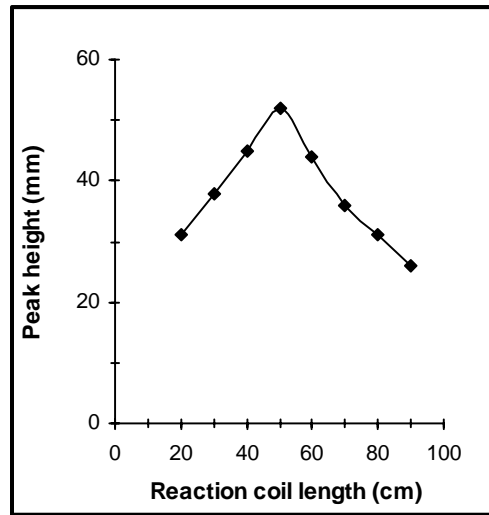


Fig.(6) Effect of Reaction coil Length

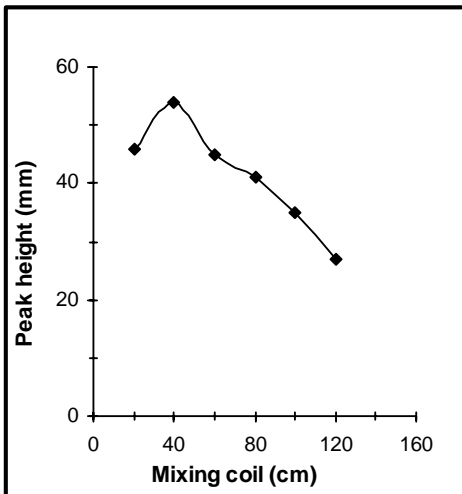


Fig.(7) Effect of Mixing coil length

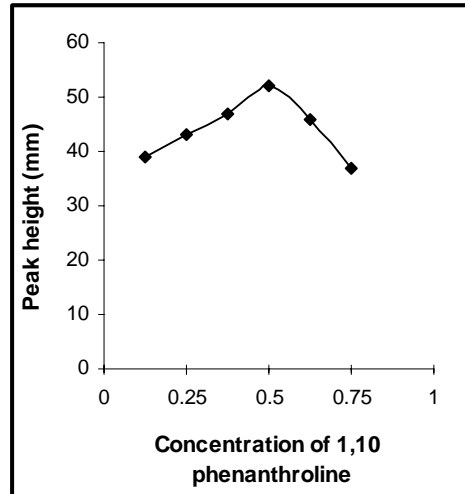


Fig.(8) Effect of 1,10 phenanthroline

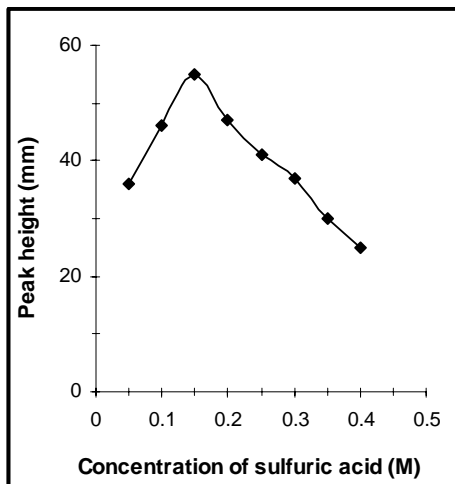


Fig.(9) Effect of Sulphuric acid

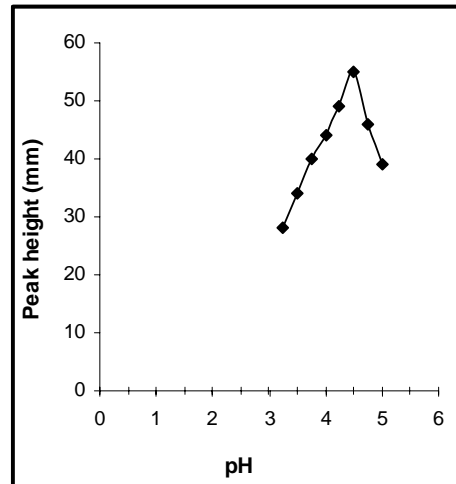


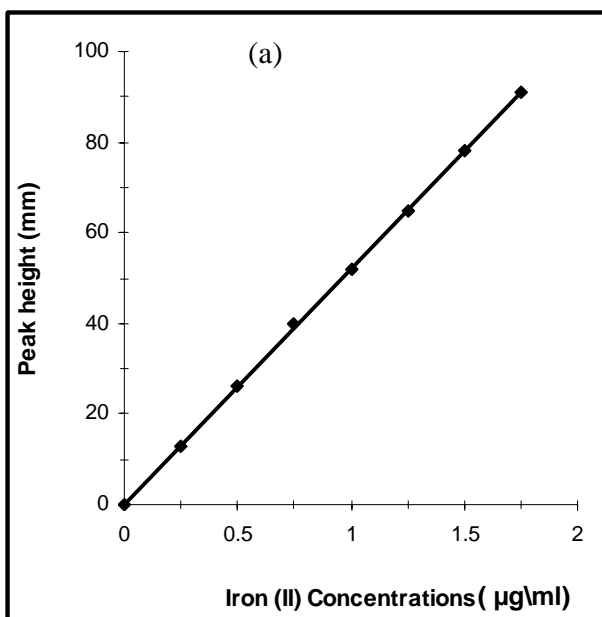
Fig.(10) Effect of pH

Standard Calibration Graph

Under the established conditions listed in Table 2 a linear calibration graph for Iron (II) was obtained over a range (0.25-1.75 µg/ml).Figure 11 shows the calibration graph and the recording peak height for series of iron (II) standard. The linear graph has a regression coefficient of 0.9999,the detection limit (2×noise) was 0.1 µg/ml and the relative standard deviation (R.S.D%) for ten replicates of (1.0 µg/ml) iron (II) was 0.1% and the sample throughput was 108 sample/h.

Table (2) Optimum conditions for Iron (II) determination by FIA

Parameters	Value
sample volume (µl)	90
Flow rate (ml\min)	0.8
Total flow rate (ml\min)	2.0
Reaction coil length (cm)	50
Mixing coil length (cm)	40
1,10 Phenanthroline conc. (% w\ v)	0.5
Sulphuric acid Conc.(M)	0.15
pH	4.5



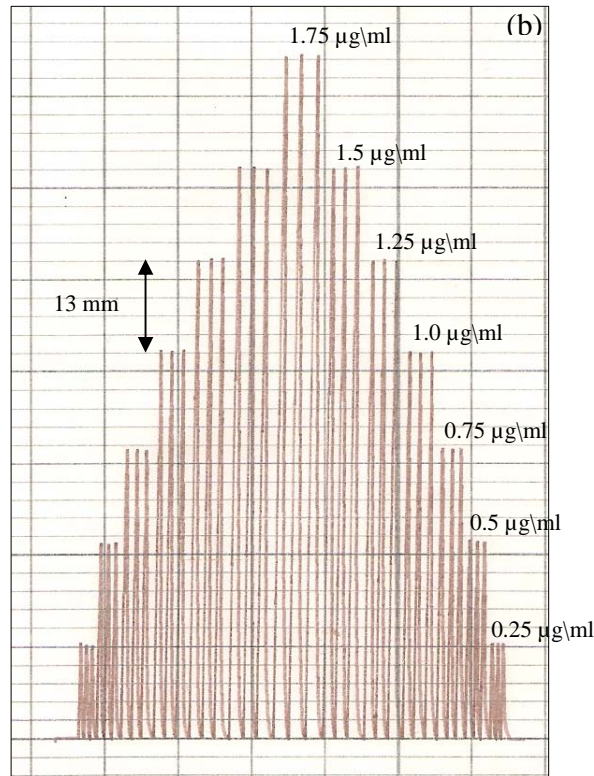


Fig.11(a) Standard calibration graph of Iron (II) .
 (b) Peaks obtained by injected Iron (II) in concentration range shown above.

Iron (II) concentrations in water:

Table 3 and figures (12-20) indicated that the average of iron (II) concentrations in study region increasing from north (station 1) to the south (station 9). This increasing manner in Shatt Al-Arab river was reported by many researchers (Al-Immara et al.2000, Al-Muddafer et al.1992). This increasing may be thought to be due to urbanization contributed industry and the iron release due to corrosion from wreckages in Shatt Al-Arab river, which can be pointed as the main sources of iron (II) in Shatt Al-Arab water.

The average of iron (II) also, increase during winter season due to rainwater percolating through soil and rock dissolves minerals containing iron and hold in natural water of Shatt Al-Arab (Anduc et al 2009).

So, in general the average of iron (II) concentration in Shatt Al-Arab water, which is the main source of drinking water in basrah province higher than the concentration limit (0.3-1.0 µg/ml) reported World Health Organization (WHO 1998) Finally, using a semi-automated flow injection spectrophotometric method provide a sensitive, precise, and sample throughput for determination the level of iron (II) in Shatt Al-Arab water.

Table (3) Concentrations of Iron (II) ($\mu\text{g/ml}$) in water for period oct.2009 to sep.2010

St .	Concentrations of Iron (II)											
	Oct 2009	Nov 2009	Dec 2009	Jan 2010	Feb 2010	Mar 2010	Apr 2010	May 2010	Jun 2010	July 2010	Aug 2010	Sep 2010
1	0.30	0.45	0.95	0.80	0.70	0.40	0.30	0.30	0.45	0.50	0.60	0.80
2	0.30	0.60	1.0	1.20	1.25	0.45	0.20	0.30	0.55	0.55	0.50	0.65
3	0.40	0.50	1.25	1.35	0.85	0.35	0.25	0.30	0.40	0.50	0.35	0.55
4	0.25	0.35	0.90	1.30	0.75	0.40	0.30	0.35	0.25	0.35	0.40	0.65
5	0.35	0.55	0.95	1.40	0.95	0.85	0.45	0.45	0.40	0.45	0.75	0.85
6	0.30	0.75	1.0	1.45	1.20	0.80	0.40	0.35	0.55	0.50	0.65	0.60
7	0.95	0.90	1.50	1.55	1.30	0.60	0.35	0.30	0.50	0.55	0.60	0.55
8	1.0	0.65	1.65	1.50	1.25	0.75	0.40	0.35	0.60	0.65	0.80	0.85
9	1.25	1.30	1.55	1.65	1.45	0.90	0.40	0.45	0.60	0.75	0.80	0.80

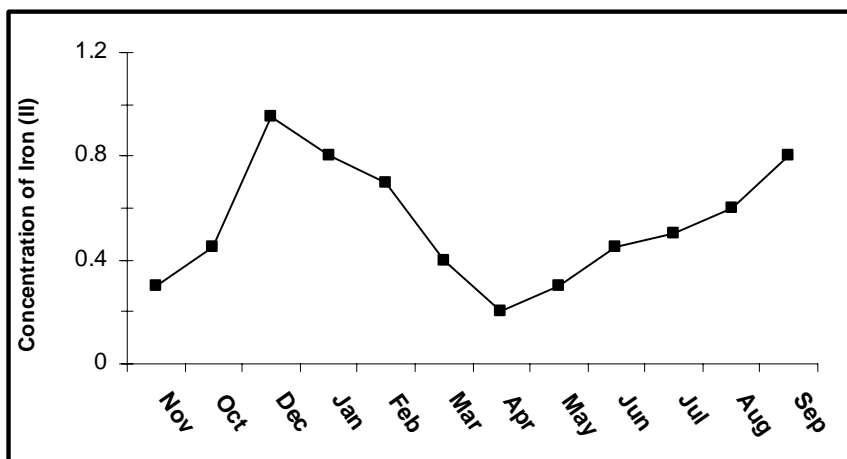


Fig.(12) Monthly variation for iron (II) in the station 1(Qurnah (Tigris))

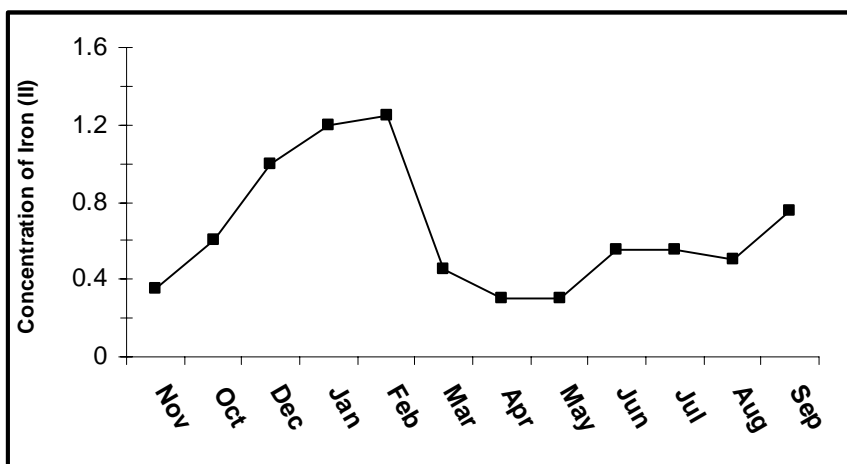


Fig.(13) Monthly variation for iron (II) in the station 2 Qurnah (Euphrates)

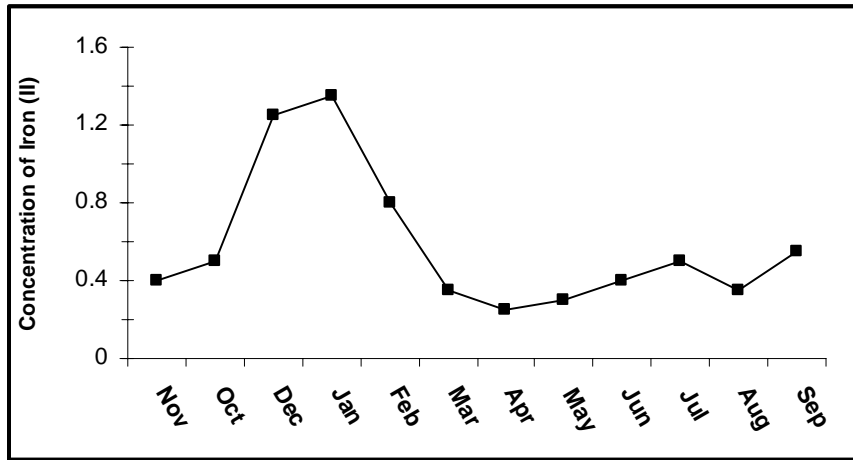


Fig.(14) Monthly variation for iron (II) in the station 3 (Saad bridge)

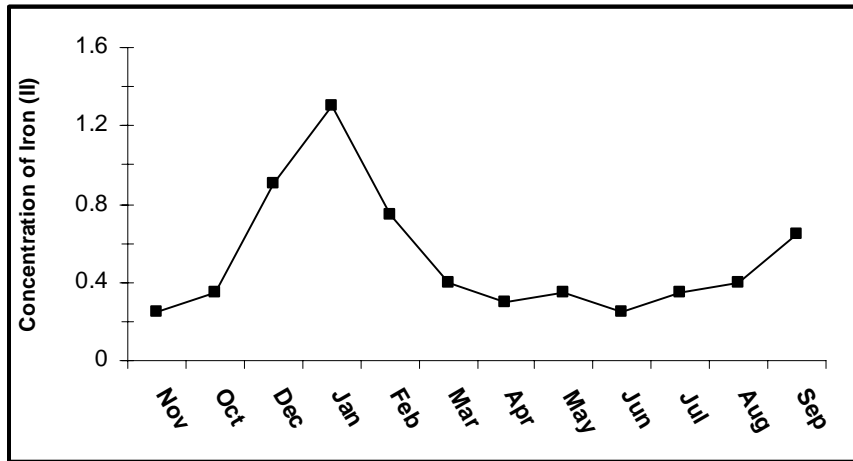


Fig.(15) Monthly variation for iron (II) in the station 4 (Qarmat Ali)

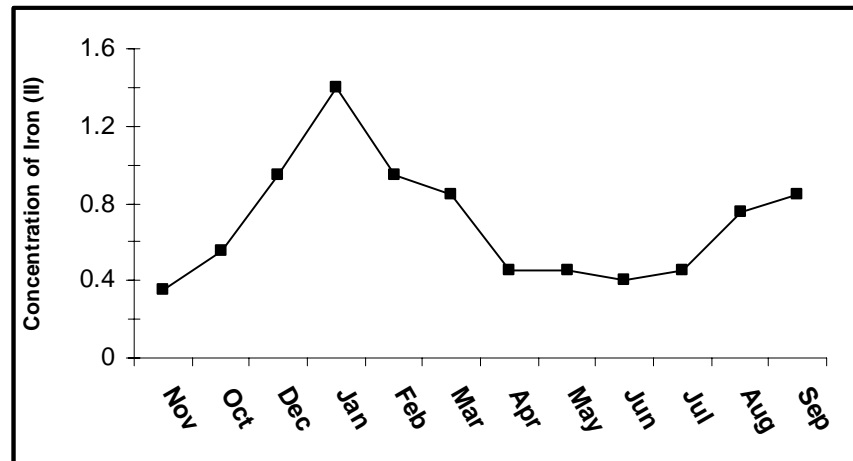


Fig.(16) Monthly variation for iron (II) in the station 5 (Al-Najeebia)

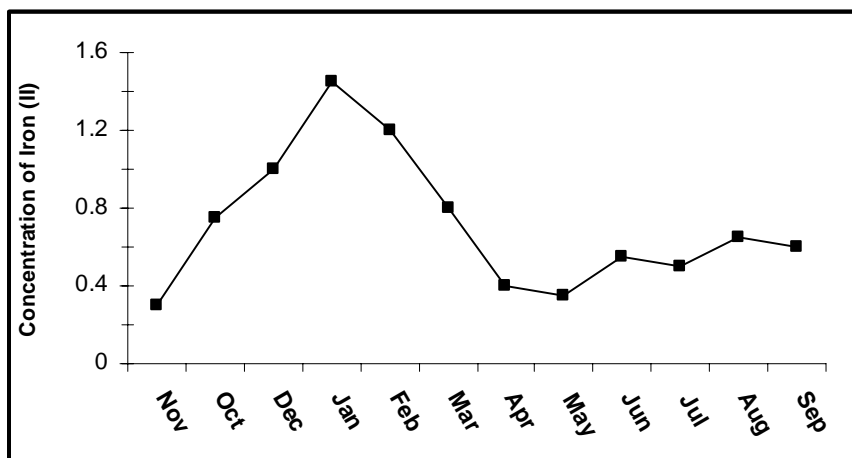


Fig.(17) Monthly variation for iron (II) in the station 6 (Ashar)

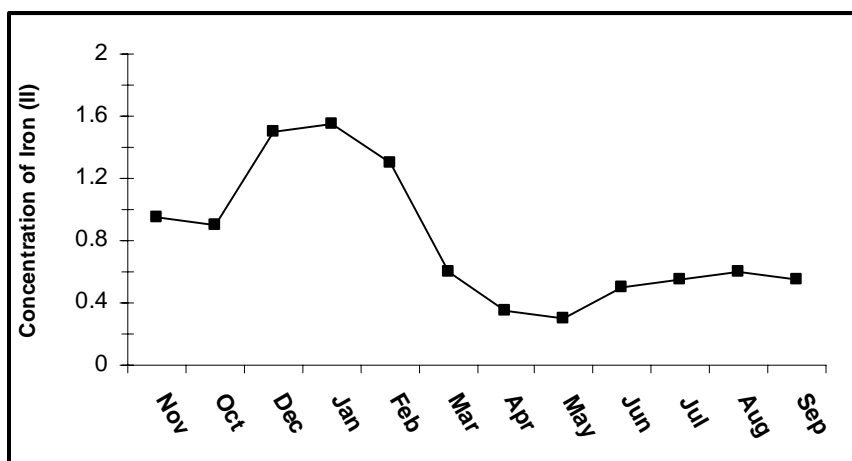


Fig.(18) Monthly variation for iron (II) in the station 7 (Abu Al-khasib)

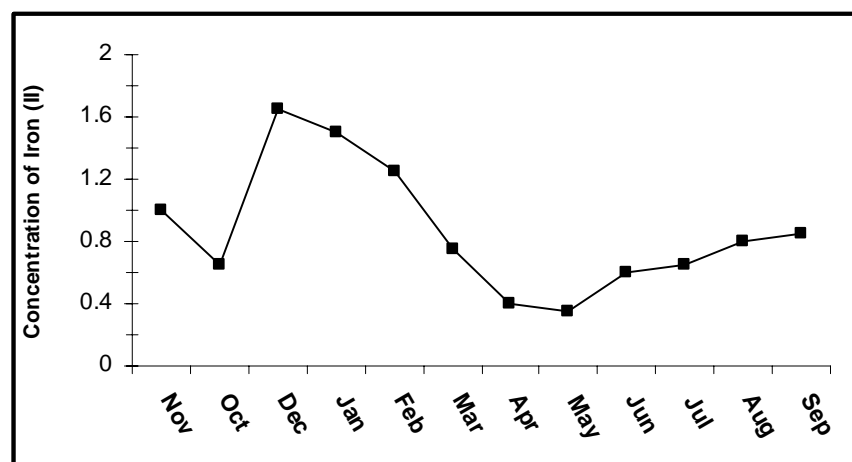


Fig.(19) Monthly variation for iron (II) in the station 8 (Al-Seeba)

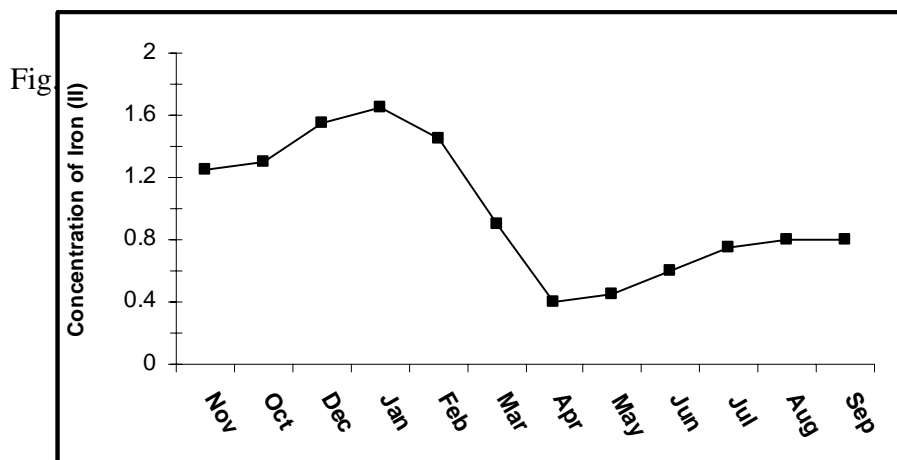


Fig.(20) Monthly variation for iron (II) in the station 9 (Al-Fao)

Table(4) Seasonal average for Iron (II) concentrations (µg\ ml) in the study period

Stations	Autman 2009	Winter 2010	Spring 2010	Summer 2010
1	0.375	0.80	0.3	0.783
2	0.65	1.15	0.3	0.580
3	0.45	1.15	0.3	0.45
4	0.30	0.98	0.35	0.40
5	0.45	1.10	0.585	0.60
6	0.525	1.20	0.50	0.575
7	0.925	1.45	0.415	0.55
8	0.825	1.45	0.50	0.725
9	1.275	1.55	0.585	0.725

Conclusion

A home-made semi-automated FI spectrophotometric provides simple, fast, reproducible and sensitive mean for determination of Iron (II) levels in Shatt Al-Arab water.

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