Determination of some Nitrogen and phosphorous species in Shatt Al-Arab River by flow injection analysis

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Abstract:

FIA is a very successful method in simplifying chemical assays. The main reasons for the success are the following advantage of FIA over conventional manual techniques: High sampling rate, smaller sample and reagent consumption and waste generation, simplicity and low cost instrumentation, Availablability of instrumentation in all laboratories, increased precision compared to batch methodologies and Automation in sample preparation and detection.

A Study was conducted monthly to estimate the levels of some nitrogen and phosphorous species : Nitrite (NO_2^-), Nitrate (NO_3^-) Ammonium (NH_4^+) and phosphate (PO_4^{-3})   in waters of shatt Al-Arab from nine stations: (1) Qurnah\ (Tigris) (2) Qurnah \Euphrates (3) Saad bridge (4) Qarmat Ali (5) Al-Najeebia(6) Ashar(7) Abu Al-khasib(8) Seeba and (9) Fao for the period October 2009 to September 2010. The higher concentrations of nitrite were recorded in the station 5 (Al-Najeebia) in march 2010 was 0.110 μg\ml and station 8) Seeba(in Jan 2010 was 0.095 μg\ml while the higher concentrations of Nitrate were recorded in station 7 (Abu Al-khasib) in Jun, July 2010 were 0.225,0.275 μg\ml respectively. The results indicated that (NH_4^+) concentrations increasing during May, June and July 2010 especially in stations 5 and 6 was (0.95, 1.35),(1.30, 1.25) and (1.45, 1.40 μg\ml) respectively. phosphate concentrations increasing during winter and spring 2010 especially in stations (Ashar, Abu Al-Khasib, Seeba,and Fao) 1.566, 2.033, 0.966, 1.266 μg\ml respectively. This can be attributed to increasing in temperature in summer, salinity of Shatt Al-Arab water and decay of organic and inorganic compounds in high temperature.
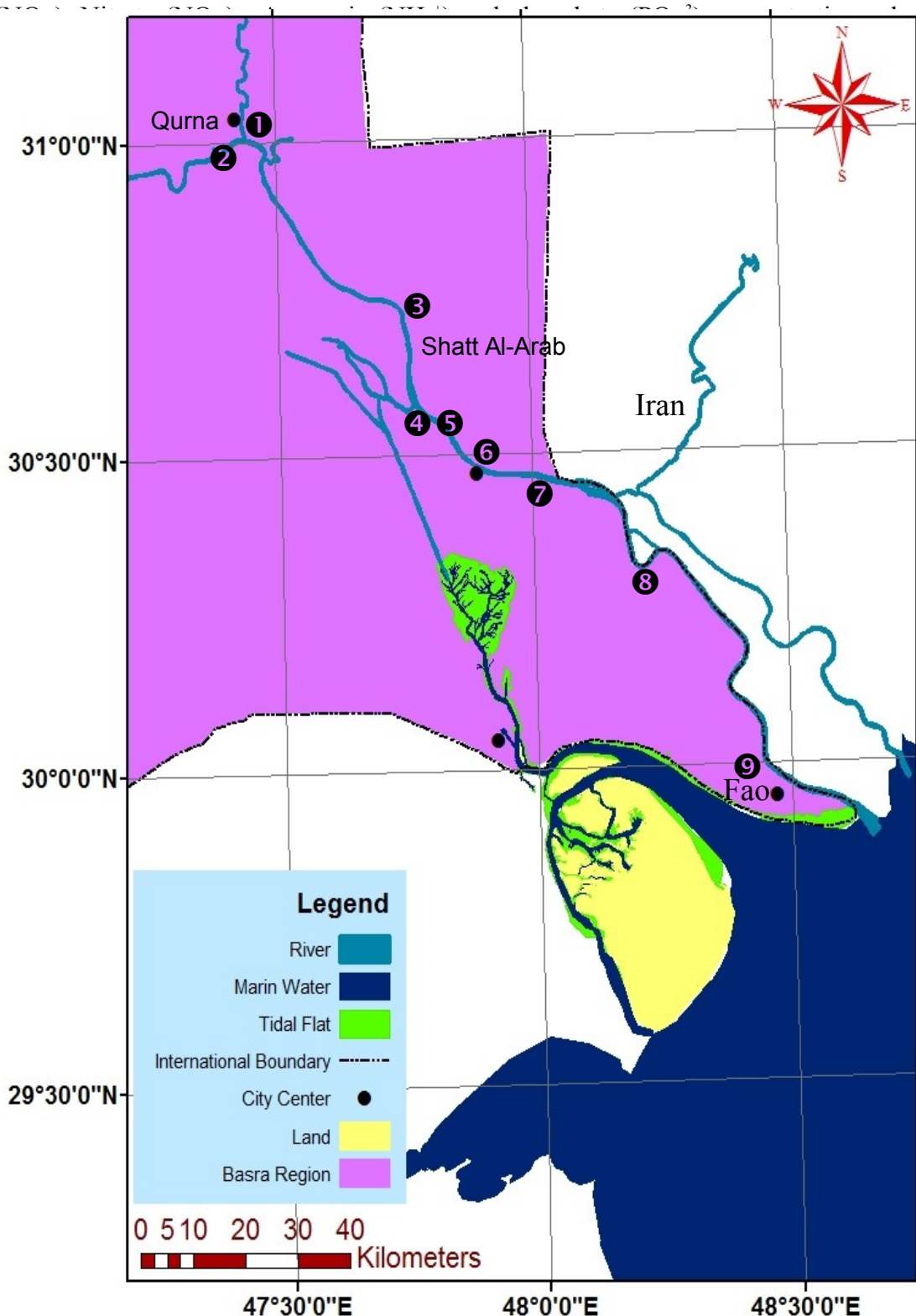
Introduction

Waters are an important factor in ecological balance and their pollution is a major and actual problem with diverse consequences of a human population (Miller and Tyler,2002). Nitrogen and phosphorous are considered major nutrients because they are essential to the growth of plants (Metcalf,1991). There are different forms of nitrogen and phosphorous found in water ,in this case the forms that will be studied are the Nitrite (NO_2^-), Nitrate (NO_3^-) ,Ammonia (NH_4^+) and phosphate (PO_4^{-3}) ions. Nitrite (NO_2^-) and Nitrate (NO_3^-) are an important analytes for the environmental problem and human health and its detection and quantification are essential (Hisakasu,2000). Nitrite appear as intermediates in the nitrogen cycle, it can be formed by the oxidation of ammonia of or the reduction of nitrate (Wetzel and Linkens,2000). Nitrite can enter through the use of corrosion inhibitors in industrial process water , or through the conversion from ammonia or nitrate (Pacheco and Cabrera,1997). Generally, nitrate is found in much higher concentration than nitrite in water. Since, nitrate are the most stable with the ratio of the tow dependent on factors such as acidity and temperature (Bruning and Kaneene,1993). Source of nitrate that can enter in water include fertilizer, septic system, industrial waste and food processing waste (Gelberg et al.1999) ,activities near the water can potentially contaminate the water supply   (Dobson and Fride,1998). Nitrite (NO_2^-) and Nitrate (NO_3^-) ions are hazardous materials that naturally occure in natural water (Craun et al.1981). Ammonia nitrogen in water comprised of dissociated ammonium (NH_4^+) and gaseous ammonia. The ratio of both forms depends on pH and the temperature of water (Quinn,1996). Ammonia is part of natural nitrogen cycle. It is released to the environmental by natural processes such as the decomposition of nitrogen matter, human and animal excrements. It can also be released to the environmental by extensive use of fertilizers in agriculture, sewage water, spillage or leakage from wastewater treatment plants (Jeffrey,1995). Phosphate is considered as the growth limiting nutrient for plant and microbial growth (Munoz et al.1997),and responsible of controlling fresh water and terrestrial ecosystem productivity (Zhang et al.1998). Phosphate sources include runoff from agricultural sites, fertilizer, and sewage (Kiely,1997). The presence of nutrients in water increases the growth of plants and this means food for higher organisms, increasing fish population and biological diversity. Excessive concentrations of nitrate and phosphate will an imbalance or instability in ecosystem, causing Eutrophication in the water (Conrath et al. 1995).

Several analytical methods for nitrite (NO_2^-), nitrate (NO_3^-), ammonia (NH_4^+) and phosphate(PO_4^{-3}) determination in water have been reported including spectrophotometry (Ahmed et al.1996, Reis et.al,1992, Joaquim and Antonio 1995) Chemiluminescence (Garside,1982) Electrophoresis (Okemgbo et al.1999) Florescence spectroscopy (Massaging and Fanning,2000 ,Roslyn *et al.*, 2004) Voltametry (Fogg and Bsebsu,1982) and Ion Chromatography (Ito et al.2005,Gibb et al., 1995). FIA is a very successful method in simplifying chemical assays. The main reasons for the success are the following

advantage of FIA over conventional manual techniques: Reduced labour costs due to automation ,Great precision due to mechanical performance of the assays, High sampling rate, Smaller sample and reagent consumption and waste generation, Simplicity and low cost instrumentation, Availablability of instrumentation in all laboratories, Reduced analysis cost when a lot of samples have to be analyzed, Increased precision compared to batch methodologies and Automation in sample preparation and detection. (Ruzicka and Hansen,2005, Trojanowicz,2006).

Many studies were conducted for the estimation of nitrite, nitrate, ammonia and phosphate by flow injection analysis in the Shatt Al-Arab river among which are Al-Maliki,1999, Al-Sowdani et al.1999, Gihlim,2001 and Al-Jorany 2008. The objectives of this study was to evaluate changes in Nitrite (NO_2), Nitrate (NO_3), ammonia (NH_4) and phosphate (PO_4^{3}) concentrations along Shatt Al-Arab ...od.

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Fig. (1) Map of Shatt Al-Arab River and sampling Locations.

Reagents and solutions:

All reagents were analytical (grade),Nitrite standard solution (400 µg ml^{-1}): 0.15g of Sodium nitrite NaNO$_2$ was dissolved in 250 ml of deionized water. The working and standards solutions over the rang

0.02-1.2 µg ml^{-1} were prepared by serial dilution of stock solution. Sulphanilamid Solution (1.0%w\v): 2.5g of Sulphanilamid was dissolved in 130 ml conc. hydrochloric acid and made up to 250 ml with deionized water. N-(1-Nphthyl) ethylene diamine dihydrochlorid solution (0.3%w\v): 1.5g of N-(1-Nphthyl) ethylene diamine dihydrochlorid was dissolved in 500 ml deionized water. Nitrate standard solution (400 µg ml^{-1}): 0.137g of sodium nitrate $NaNO_3$ was Dissolved in 250 ml of deionized water. The working and standards solutions over the rang 0.05-0.3 µg ml^{-1} were prepared by serial dilution of stock solution.

100 µg\ml Ammonium standard solution was prepared by dissolving 0.3818 g of ammonium chloride in 1L of deionized water. The standards and working solutions were prepared by serial dilution of stock solution. Nessler's reagent was prepared by dissolving 14g of potassium iodide in 40 ml of deionized water (solution 1) and 4g of mercuric chloride in 100 ml of deionized water (solution 2), solution 1 is added in to solution 2 with continuous stirring until a slight red precipitate is formed then 100ml of 10N of sodium hydroxid is added into solution and made up to 500ml with deionized water. (2N) Sodium hydroxide was prepared by dissolving 20g 1n 250ml of deionized water, then 0.8N is prepared by dilution.

Phosphate standard solution (100 µg ml^{-1}): Potassium dihydrogene phosphate KH_2PO_4 is dried in an oven at 110°C. Exactly 0.1432g was dissolved in 1L of deionized distilled water. Phosphate standard over the rang 0.5-2.5 µg ml^{-1} were prepared by serial dilution in distilled water. Ascorbic acid solution (2.5 %w/v) : 25g of ascorbic acid was dissolved in 1L of deionized distilled water which 10 ml of glycerin was added to it. Ammonium Molybdate solution ($6×10^{-3}$ M): 7.4154g of ammonium Molybdate was dissolved in 1L of 0.4 M nitric acid which was prepared by dilution of 25 ml of concentrated nitric acid in 1L of water.

Procedures

The flow manifolds used for NO_2^-, NO_3^-, NH_4^+ and PO_4^{-3} are shown in Figs. 3,4,5 and 6 respectively. The carrier stream and reagents were pumped at suitable rates. An optimum volume in microliter was injected by rotary injection valve. 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 formed complexes were measured at selected wavelength to each NO_2^-, NO_3^- and NH_4^+ by spectrophotometer equipped with flow cell. The recorded peak heights can be related to the sample concentrations.

Apparatus

A schematic diagram of Home-made flow injection analysis (FIA) system established in marine science center, marine chemistry department used in this study is shown in Figs.3,4,5 and 6. A peristalatic pump (Auto-analyzer) with constant speed (16.7 cycle\min) was used for propelling a carrier solution (CS) and reagent solutions (R1, R2). A six- way valve (RHEODYNE, Catati,

California, USA) were used for introducing the standards and samples into the carrier stream. The absorbance was measured with spectrophotometer (shimadzu, UV-150.Japan) equipped with 200µl 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 remainder of the manifold. All results are the mean of six injections of the natural water samples.
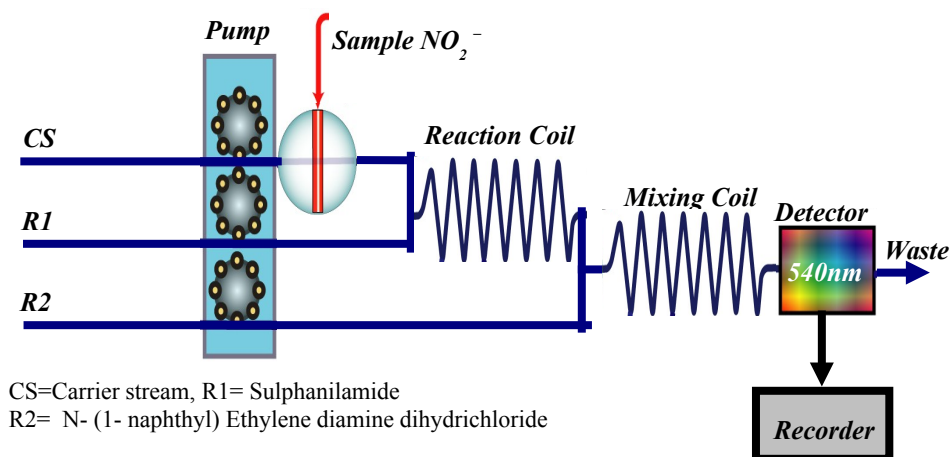
CS=Carrier stream, R1= Sulphanilamide
R2= N- (1- naphthyl) Ethylene diamine dihydrichloride

Fig 2 Manifold for determination of nitrite NO_2^- in water by FIA

CS= Carrier stream, R_1 = Sulphanilamide
R_2 = N- (1- naphthyl) Ethylene diamine dihydrochloride
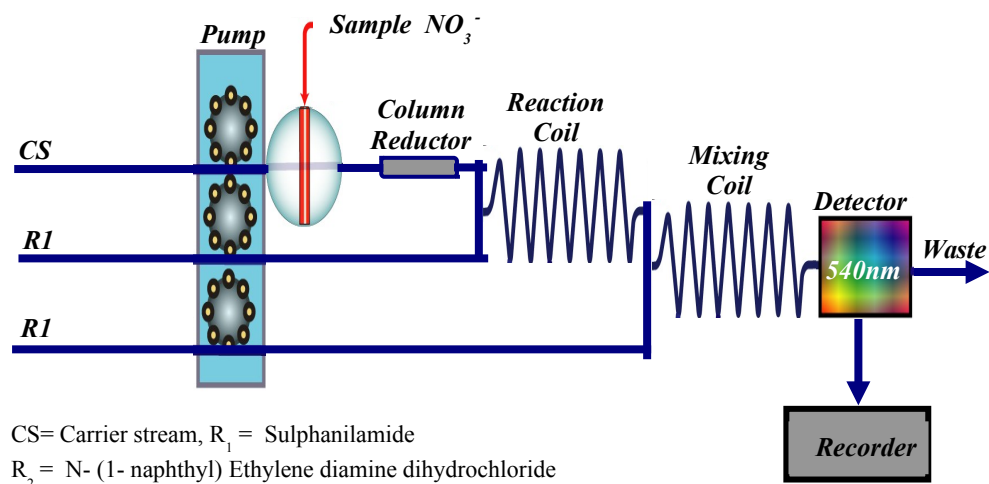
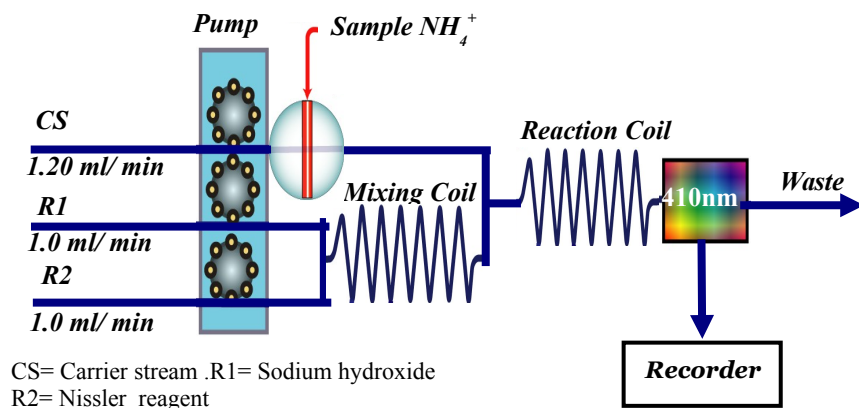Fig.3 Manifold for determination of nitrate NO_3^- in water by FIA

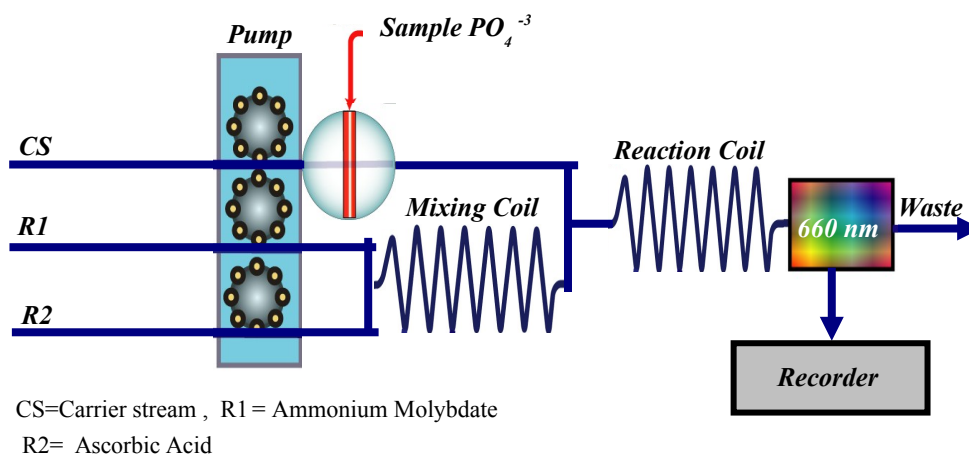Fig.4 Manifold for determination of Ammonia NH_4^+ in water by FIA

Fig.5 Manifold for determination of Phosphate in water by FIA

RESULTS AND DISCUSSION

The chemicals and physical flow injection variable should be optimized in order to make FIA units suitable to get the best results for determination of nitrite,nitrate,ammonia and phosphate. Table 2 summarizes these optimum conditions which have been used for the determination of nitrite, nitrate, ammonia and phosphate concentrations as a chemical parameters for the semi-automated FIA system:

Table 2 The optimum conditions for the determination of NO_2^-, NO_3^-,PO_4^{-3} by FIA.

Parameters	NO_2^-	NO_3^-	NH_4^+	PO_4^{-3}
Sample volume (µl)	100	100	80	90
Reaction coil length (cm)	60	60	60	50
Mixing coil length (cm)	60	60	50	50
Flow rate (ml\min)	1.0	1.0	1.20	0.60
Total flow rate (ml\min)	3.40	3.40	3.20	2.0
Column reductor length (cm)	-	7	-	-
Conc. of Ascorbic acid (w\v%)	-	-	-	0.6
Conc. of Ammonium molybdate (M)	-	-	-	$3×10^{-3}$
Conc. of sulphanilamid (w\v%)	0.25	0.25	-	-
Conc. of NED (w\v%)	0.150	0.150	-	-
Nessler reagent conc.(%w/v)	-	-	12.0	-
Sodium hydroxide conc.(N)	-	-	1.25	-
Linearity (µg/ml)	00.2-0.12	0.05-0.3	0.25-1.5	0.5-2.5
Detection limit (2×noise) (µg/ml)	0.009	0.01	0.1	0.1
R.S.D%	0.379	0.432	0.1	0.673
Regression coefficient	0.9999	0.9999	0.9998	0.9999
Sample throughput (sample\h)	120	96	108	108

NED= N-(1-naphthyl) ethylene diamine dihydrochloride

Nitrite and Nitrate concentrations in Shatt Al-Arab water:

Nitrite and Nitrate concentrations ranged from 0.02-0.11 µg\ml and 0.02-0.275 µg\ml respectively. Variation in ammonium concentration was between 0.2-1.45 µg\ml.The highest concentrations of nitrite and nitrate were measured during February 2010 and July 2010 respectively whereas the lowest concentrations were recorded during August 2010 and December-January 2010 for nitrite and nitrate respectively (Fig.6 and 7). The highest concentration of ammonium was recorded during July 2010,whereas the lowest concentrations were recorded during February 2010 (Fig.8)

Nitrate is found in much higher concentration than nitrite in water. The Figures (6 and 7) show the monthly variations of NO_2^- and NO_3^- concentrations during the study period which were obtained by the semi-automated FIA spectrophotometeric method.

 The results point clearly that the level of NO_2^- concentrations decreasing during the study period. This can be attributed to increasing in temperature degree 26-34 C˚ which may lead to oxidation of nitrite (NO_2^-) to nitrate (NO_3^-) and consumption of nitrogen compounds by phytoplankton. The higher concentrations of NO_2^- were recorded in the station 5 (Al-Najeebia) in the February 2010 was 0.110 µg\ml and Station 8 (Al-seeba) in January 2010 was 0.095 µg\ml. This can be attributed to the waste of Al-Najeebia electricity station and Abadan refinery. Generally, the higher concentrations of nitrite

was recorded in winter 2010 comparative   with the other seasons (Table 3). The level of NO_3^- concentrations increasing in summer of 2010 and autumn 2010 which thought due to increasing in temperature   26-34 C°. The reversible relationship between NO_2^- and NO_3^- concentrations can be clearly indicated during summer season which thought to be due to increasing in temperature lead simply to oxidation of NO_2^- to NO_3^-.

The problem of increasing in the salinity of Shatt Al-Arab water which can be indicated from increasing of the EC from 4.68-37.2 mS\cm especially in the stations 8 and 9 (seeba and fao) during the study period, may lead to decrease of NO_3^- level in winter 2010 and spring of 2010 which was previously reported by (Abaychi et al.1988). Generally, the higher concentrations of nitrate was recorded in summer 2010 comparative with the other seasons (Table 3).

Figure 8 show the monthly variations of ammonium ion (NH_4^+**)** concentrations during the study period from October 2009 to September 2010 which were obtained by the semi-automated FIA spectrophotometeric method. The results indicated that (NH_4^+) concentrations increasing during May, June and July 2010 especially in stations 6 and 7 was (0.95, 1.35),(1.30, 1.25) and (1.45, 1.40 µg\ml) respectively. These results are more than what previously reported by (Al-Malki, 1999, Douabul et al 1987). These results may be thought due to the decay of organic and inorganic compounds in high temperature (26-34C°), then liberation of ammonium (Maulood et al. 1981) and these elevated values are due to untreated sewage which contains considerable amounts of detergents and to fertilizers used in agriculture (Douabul et al 1987).

The results also show that the minimum ammonium concentrations during the monthly variations at winter (December 2009 and January, Feberuary 2010). These results may be due to decreasing in temperature then the nitrate is not oxidized to ammonium (Wetzel, 1983)   .

 So, in general the average of ammonium (NH_4^+) concentrations in Shatt Al-Arab water which is the main source of drinking water in Basrah province higher than the concentrations limit (0.5-1 µg\ml) reported world Health Organization (WHO, 1998)

Table (3) Seasonal average for NO_2^-, NO_3^- concentrations(μg\ ml) in the study period

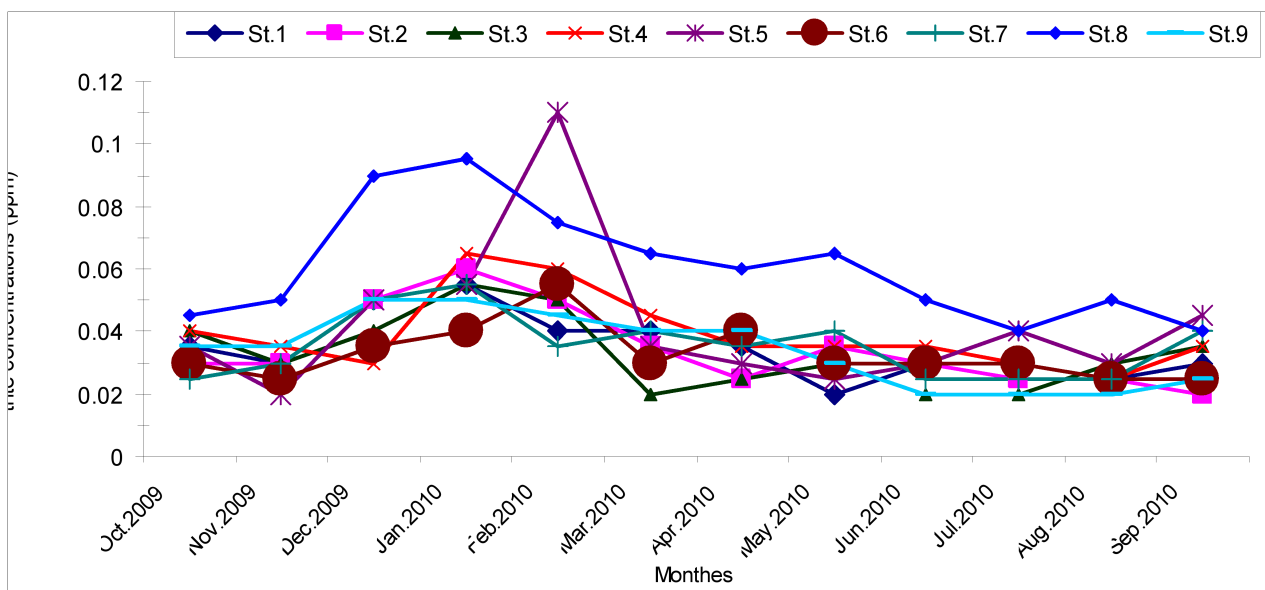| Stations	Concentrations (μg\ml)							
	Autman 2009		Winter 2010		Spring 2010		Summer 2010	
	NO_2^-	NO_3^-	NO_2^-	NO_3^-	NO_2^-	NO_3^-	NO_2^-	NO_3^-
Qurnah (Tigris)	0.0325	0.060	0.048	0.041	0.031	0.055	0.030	0.090
Qurnah (Euphrates)	0.030	0.045	0.053	0.045	0.031	0.058	0.031	0.083
Saad bridge	0.035	0.0575	0.048	0.050	0.025	0.066	0.026	0.081
Qarmat Ali	0.0375	0.0925	0.050	0.048	0.038	0.078	0.031	0.100
Al-Najeebia	0.0275	0.0875	0.071	0.060	0.030	0.100	0.036	0.116
Ashar	0.027	0.090	0.043	0.063	0.033	0.118	0.028	0.167
Abu Al-khasib	0.027	0.1275	0.046	0.071	0.038	0.111	0.023	0.217
Seeba	0.047	0.070	0.086	0.046	0.063	0.053	0.041	0.067
Fao	0.035	0.0575	0.048	0.043	0.036	0.066	0.021	0.053

Fig.6:Variation in nitrite concentrations of Shatt Al-Arab River.
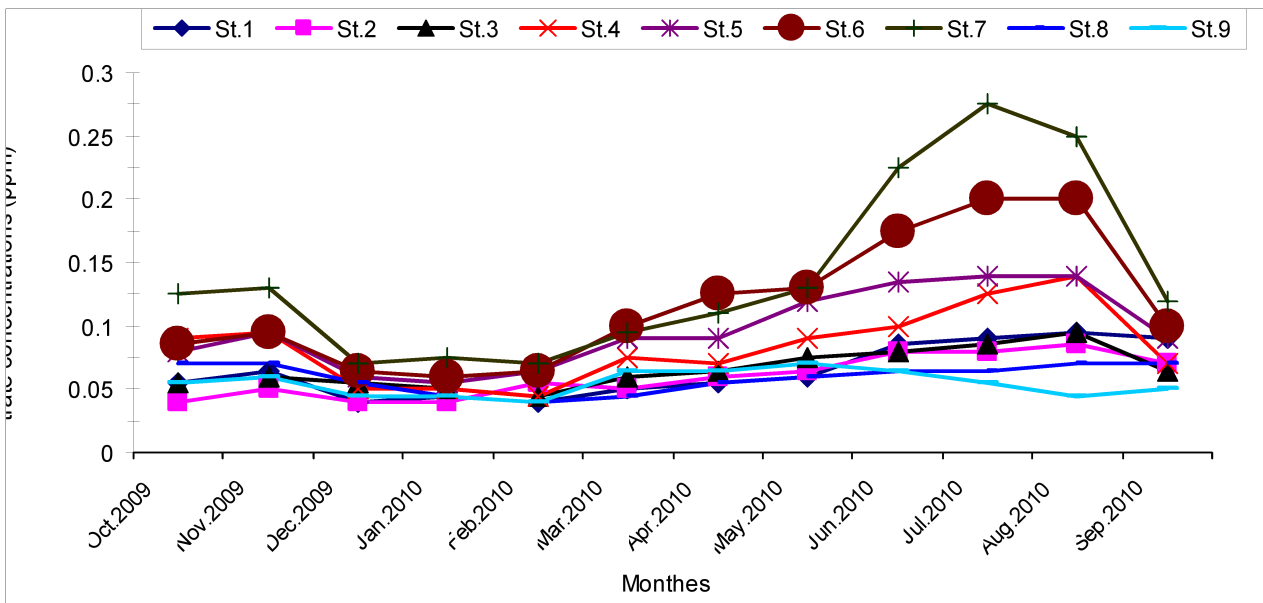
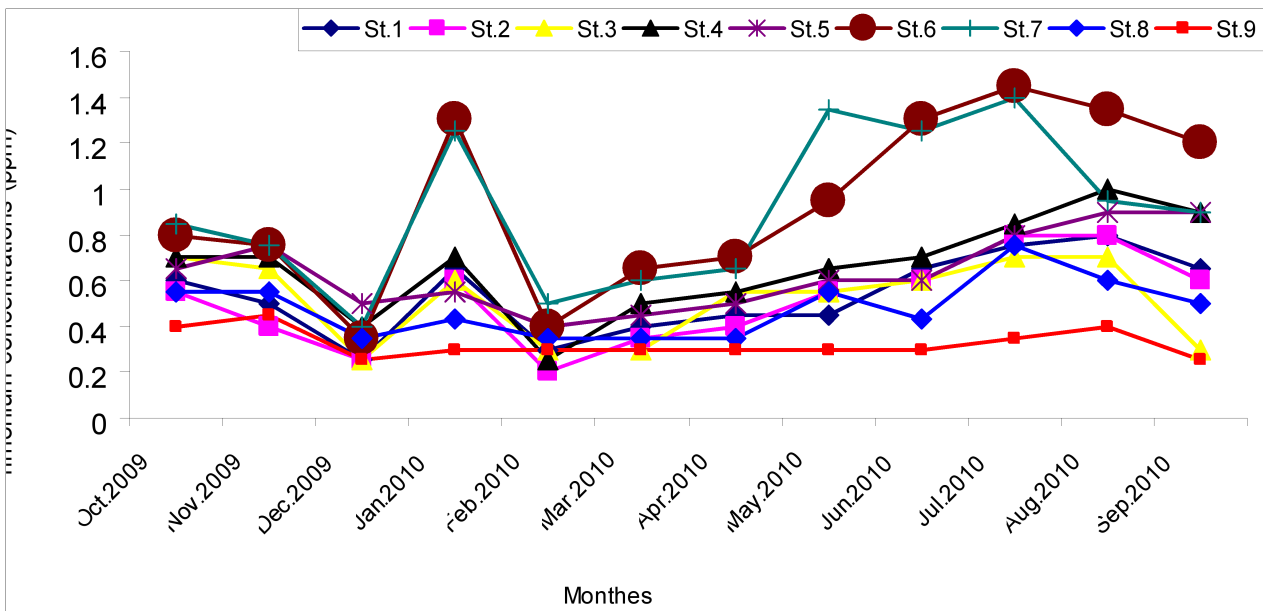Fig.7:Variation in nitrate concentrations of Shatt Al-Arab River.

Fig.8:Variation in ammonium concentrations of Shatt Al-Arab River.

phosphate concentrations in Shatt Al-Arab water:

Phosphate sources include runoff from agricultural sites, fertilizer, and sewage (Kiely.1997) Phosphate are widely used in cleaning products, toothpast,fire extinguishers, textile processing and food (Weiner et al.2001).It found in natural rivers waters and when excessive, can lead to Eutrophication in water bodies.

Figure 9 show the monthly variations of phosphate (PO_4^{-3}) concentrations during the study period which were obtained by the semi-automated FIA spectrophotometeric method. The result indicated that phosphate concentrations increasing during winter and spring 2010 especially in stations (Ashar,

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Abu Al-Khasib, Seeba,and Fao) 1.566, 2.033, 0.966, 1.266 µg\ml . These results are more than what previously reported in (Al-Shawi et al.2005,Al-Sowdani,1999). This increasing in phosphate concentrations may be due to increasing in the value of salinity which agree with what previously that increasing salinity may be lead librated phosphate from small size sediment to the water (Al- Abaychi et al.1988)
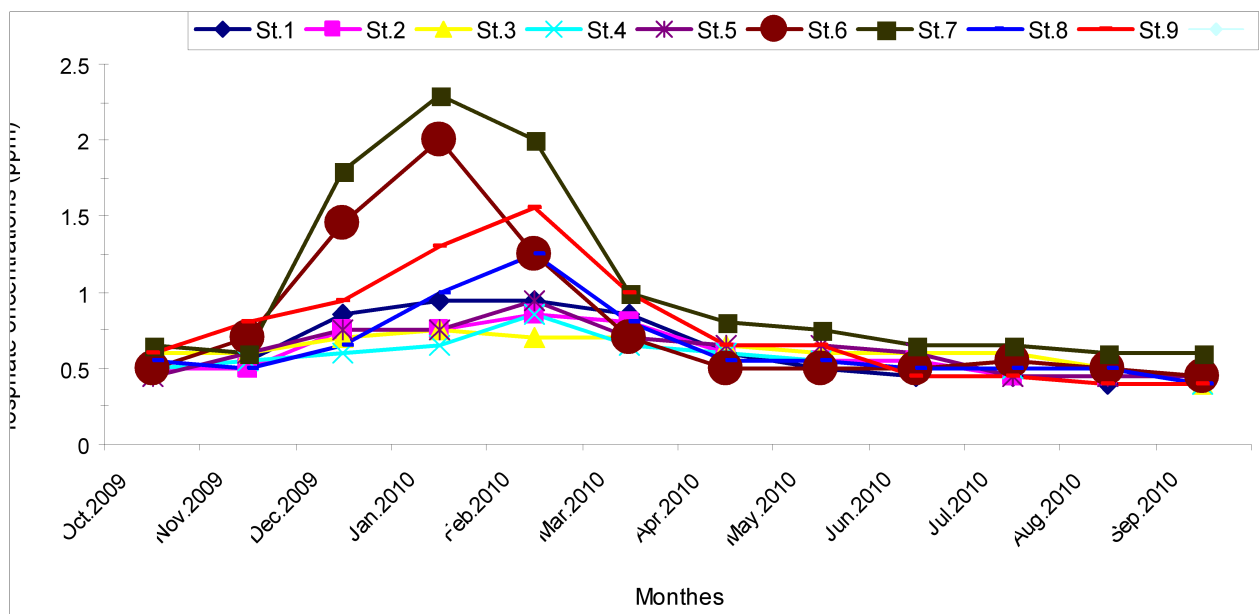

Fig.9:Variation in phosphate concentrations of Shatt Al-Arab River.

Conclusion

The FIA units were applied successfully for determination of Nitrite (NO_2^-), Nitrate (NO_3^-) ,Ammonia (NH_4^+) and phosphate (PO_4^{-3}) ions in Shatt Al-Arab river. Some of the obtained results were compared with the results of classical spectrophotometric method (APHA) as shown in the table 4. The agreement between two methods indicated clearly that the home-made semi-automated FIA units can be easily handled in routine laboratory work for determination and evaluating the pollution of Nitrite (NO_2^-), Nitrate (NO_3^-) ,Ammonia (NH_4^+) and phosphate (PO_4^{-3}) in Shatt Al-Arab water. The FIA ,also provide simple, fast, and reproducible methods for determination Nitrite (NO_2^-), Nitrate (NO_3^-) ,Ammonia (NH_4^+) and phosphate (PO_4^{-3}) in water of Shatt Al-Arab river

Table 4 comparative between FIA and classical method

Stations	January 2010 NO_2^-		January 2010 NO_3^-		January 2010 NH_4^+		January 2010 PO_4^{-3}	
	FIA	manual	FIA	manual	FIA	manual	FIA	manual
St.1	0.055	0.061	0.045	0.04	0.65	0.61	0.95	0.87
St.2	0.06	0.062	0.04	0.038	0.6	0.64	0.75	0.71
St.3	0.055	0.051	0.05	0.054	0.6	0.58	0.75	0.68
St.4	0.065	0.06	0.05	0.053	0.7	0.65	0.65	0.61
St.5	0.055	0.049	0.055	0.05	0.55	0.53	0.75	0.70
St.6	0.04	0.043	0.06	0.057	1.3	0.1	2.0	1.6
St.7	0.055	0.051	0.075	0.068	1.25	0.11	2.3	2.6
St.8	0.095	0.9	0.045	0.038	0.43	0.39	1.0	1.3
St.9	0.05	0.053	0.045	0.04	0.3	0.27	1.3	1.1
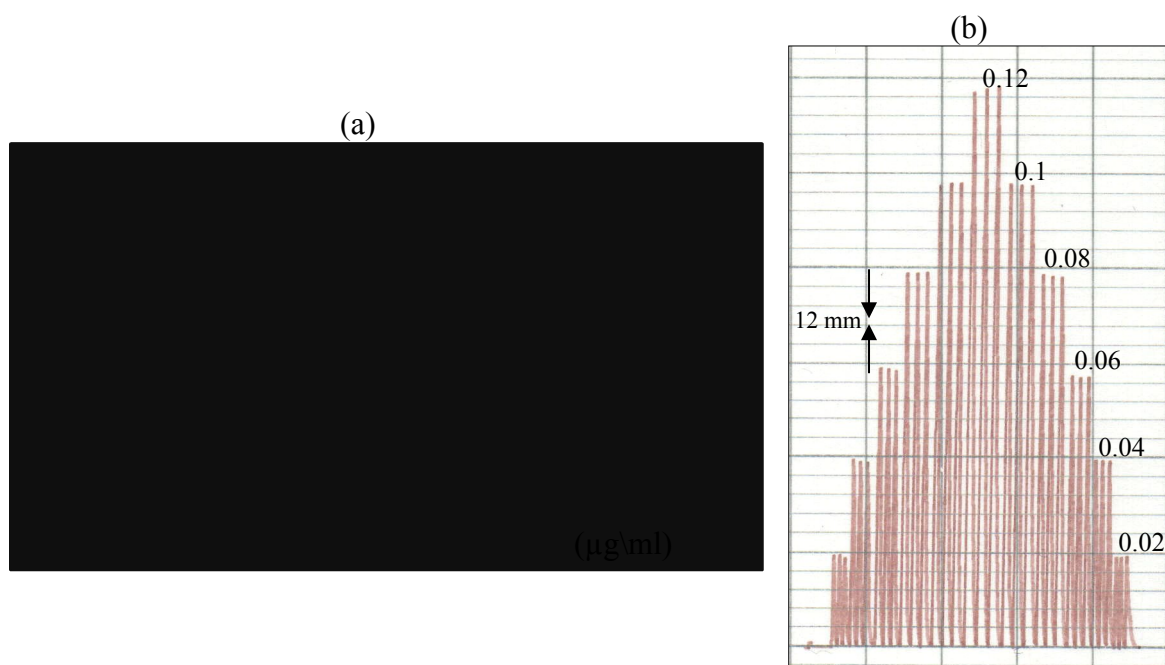
Fig.10   (a) Standard calibration graph for NO_2^- determination.
(b) peaks obtained by injected NO_2^-.

(a)

y = 301.32x
R² = 0.9999
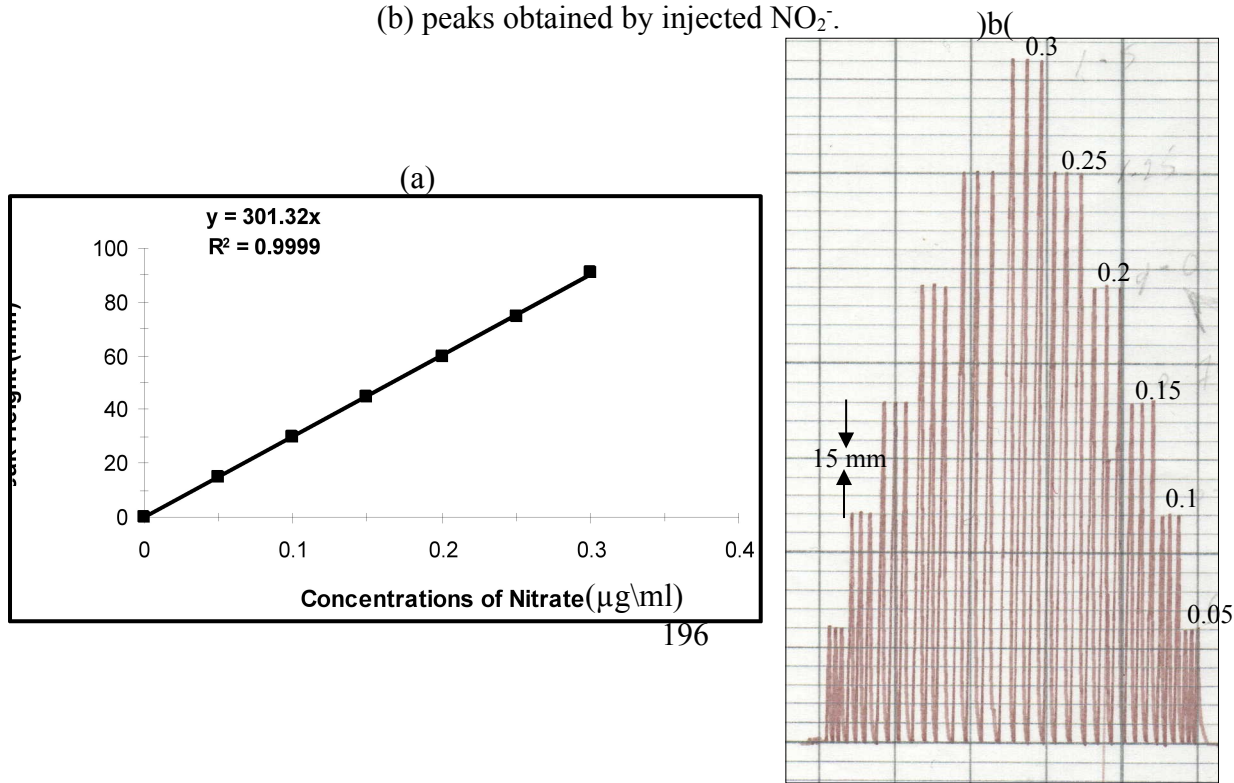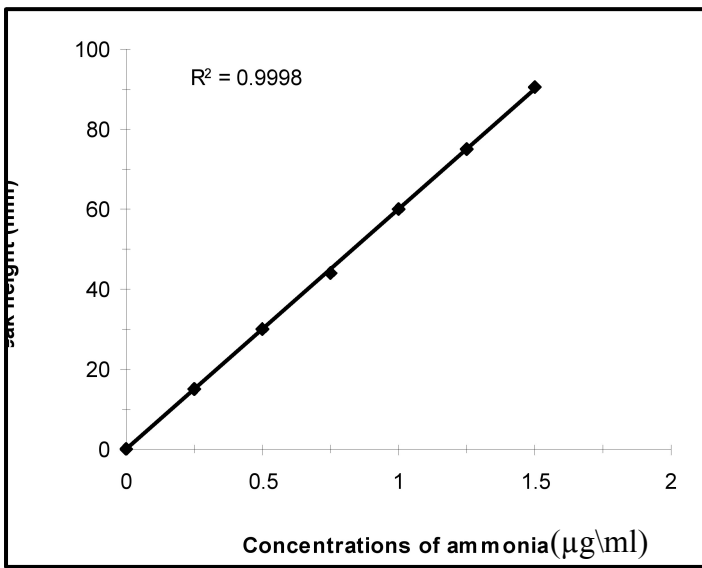
Concentrations of Nitrate(µg\ml)

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Fig.11(a)Standard calibration graph for NO_3^- determination.
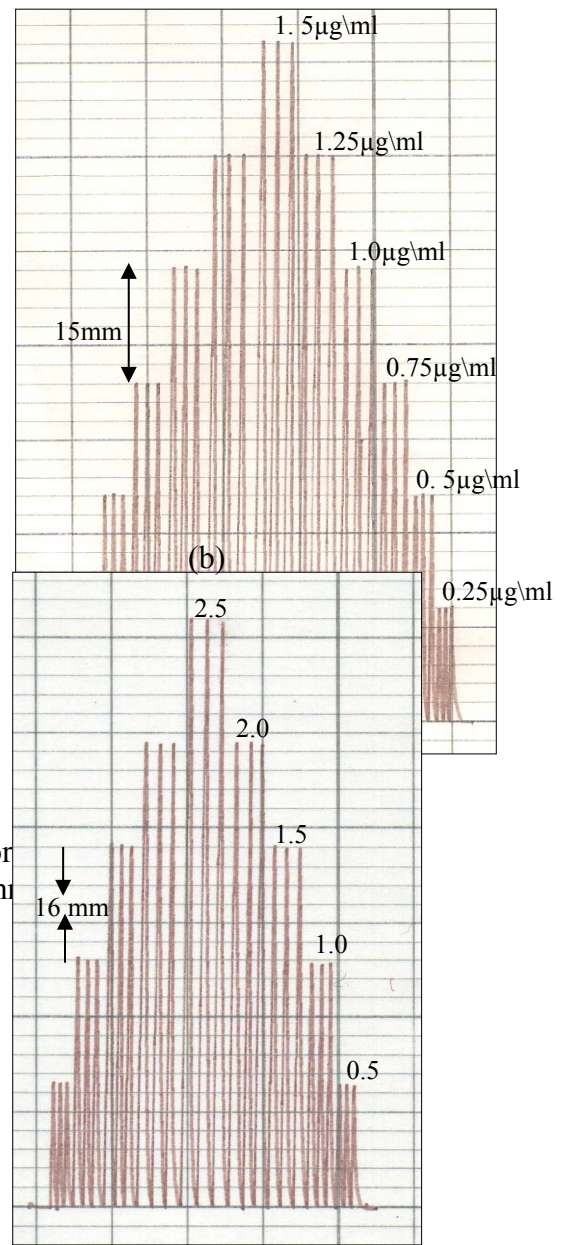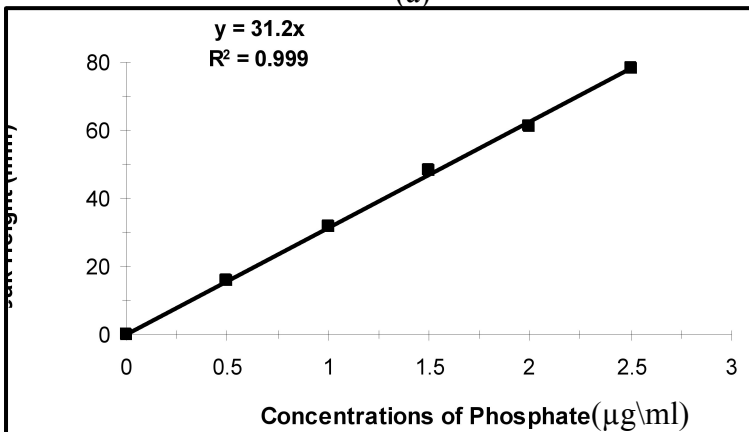(b) peaks obtained by injected NO_3^-.

(a)

(a)

(b)

Fig.12(a) Standard calibration graph for PO_4^{-3} determination.
(b) peaks obtained by injected PO_4^{-3}.

:الملخص

تقدير بعض أصناف النتروجين والفسفور في مياه شط العرب بتحليل الحقن الجرياني

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حققت تقنية الحقن الجرياني نجاحا كبيرا في مجال التحليل الكيميائي ويعود ذلك لعدة أسباب منها :سرعة النمذجة العالية،صغر النموذج والاستهلاك القليل للمحاليل، قلة تكاليف الأجهزة ،توفر الأجهزة في المختبرات والدقة العالية مقارنة مع طرق التحليل الأخرى.

سجلت الدراسة شهريا لتقييم تراكيز بعض أشكال النتروجين (النتريت،النترات والأمونيوم) والفسفور (الفوسفات) في مياه شط العرب لتسع محطات: القرنة/دجلة،القرنة /الفرات،جسر سعد،كرمة علي،النجيبية،العشار، أبو الخصيب، السيبة والفاو للفترة من تشرين الأول 2009لغاية أيلول 2010. سجلت أعلى تراكيز للنتريت في المحطة 5 (النجيبية) في آذار 2010 وكان 0.110 مايكروغرام/مل ومحطة 8 (السيبة) 0.095 مايكروغرام/مل بينما أعلى تراكيز للنترات كانت في محطة 7(أبو الخصيب)في حزيران وتموز 2010 (0.275،0.225 مايكروغرام/مل)على التوالي.وضحت النتائج أن تراكيز الأمونيوم زادت خلال مايس،حزيران وتموز 2010 خصوصا في المحطتين 5و 6 (0.95،1.35) (1.30،1.25) (1.45،1.40) على التوالي.

سجل أعلى تركيز للفوسفات خلال أشهر الربيع والشتاء 2010 في محطات (العشار،أبو الخصيب،السيبة،الفاو) وكانت 1.266،0.966،2.033،1.566 مايكروغرام/مل. أعزيت هذه النتائج الى زيادة درجة الحرارة خلال الصيف وزيادة ملوحة شط العرب وكذلك أنحلال المركبات العضوية واللأعضوية بسبب ارتفاع درجة الحرارة.

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