

Build-up a flow injection analysis unit for ammonium determination in the Shatt Al-Arab water

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(Received: 1 February 2011 - Accepted: 4 April 2011)

Abstract - A Semi- automated flow injection analysis (FIA) unit was build-up for determination of ammonium ion in water samples from the Shatt Al-Arab River during the period from October 2009 to September 2010. The ammonium concentrations in water have been measured, at each of the eight stations (Qurnah (Tigres), Qurnah (Euphrates), Saad Bridge, Garmat Ali, Ashar, Abu Al-Khaseeb, Al-Seeba and Fao), monthly. The results indicated that (NH₄⁺) concentrations increasing during May, June and July, 2010 especially in stations 5 and 6 were 0.95, 1.35 µg/ml , 1.30, 1.25 µg/ml and 1.45, 1.40 µg/ml, respectively. The FIA unit was applied successfully for the determination of ammonium in Shatt Al-Arab water sample and provide simple, fast, and reproducible methods for ammonium determination in water.

Key Words: FIA, spectrophotometer, Ammonium, Shatt Al-Arab River.

Introduction

There are several forms of nitrogen naturally existing in the environment: gaseous nitrogen, ammonia nitrogen, nitrates, nitrites and many organic compounds which are simply classified as organic nitrogen (Miller and Tyler, 2002). Ammonia nitrogen in water comprised of dissociated ammonium (NH₄⁺) 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). Various methods have been developed for quantification of ammonium concentration in different samples such as spectrophotometric (Joaquim and Antonio, 1995), Ion Chromatography (Gibb, 1995) and Fluorescence (Roslyn *et al.*, 2004).

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 (Trojanowicz, 2008). FIA system is characterized by very short time and the analytical signal is obtained with second and which leads to high sample throughput (Barnett *et al.*, 1999). In a typical basic FI analyzer the sample is injected into a carrier stream where it may react with a reagent present or additionally introduced to produce a chemical species that can be sensed by a flow-through detector positioned downstream of the injection device. A peak shaped signal is recorded as the sample zone passes

through the flowthrough detector and the peak height or peak area can be related to the analyte concentration in the original samples or standards (Ruzicka and Hanses, 2005). The aim of the present work was to establish conditions for simple, fast, and accurate flow injection spectrophotometric method determination of ammonium in natural water of Shatt Al-Arab river.

Materials and Methods

Shatt Al-Arab River originates from the junction of the Tigris and Euphrates rivers at Qurna. The length of this river is about 175 km; its width varies from 0.4km at Basrah city to 1.5 km at the river mouth. Its depth ranges from 7.5 m to 12.5 m. The Karun River joins the eastern bank of Shatt Al-Arab River south of Basrah city. Water level in the Shatt Al-Arab River is under the influence of the tide (Saad and Kell, 1975). A total of 120 samples of natural water of Shatt Al-Arab River were collected from eight stations (Qurnah (Tigris), Qurnah (Euphrates), Saad Bridge, Garmat Ali, Ashar, Abu Al-khaseeb, Al-Seeba and Fao are shown in Table (1) and Figure (1) over 12 months during the period from October 2009 to September 2010. The water samples were taken from 30 cm down the water surface and few drops of chloroform were added to the sample (APHA, 1999).

All reagents used were analytical (grade) unless otherwise stated and all stock and standard solutions were prepared in pure deionized distilled water. 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 hydroxide is added into solution and made up to 500ml with deionized water. (2N) Sodium hydroxide was prepared by dissolving 20g in 250ml of deionized water, then 0.8N is prepared by dilution.

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 Figure (2). A peristaltic 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) was used for introducing the standard ammonium and sample 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.

The flow manifolds used for NH_4^+ is shown in Figure (2). The carrier stream and reagents were pumped at suitable rates. An optimum volume in microliter was injected by rotary injection valve. Different coils lengths were inserted for mixing the reagents and reaction between the injected sample and the reagents in the flow system. The absorbances of formed complexes

were measured at selected wavelength to NH_4^+ by spectrophotometer equipped with flow cell. The recorded peak heights can be related to the sample concentrations.

Table 1. Sampling sites, Names and positions of Study area.

Stations	Sampling Point Name	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	Ashar	30°31'169"N	47°50'647"E
St.6	Abu Al-khaseeb	30°27'709"N	48°00'633"E
St.7	Al-Seeba	30°20'210"N	48°15'995"E
St.8	Fao	29°59'359"N	48°27'792"E

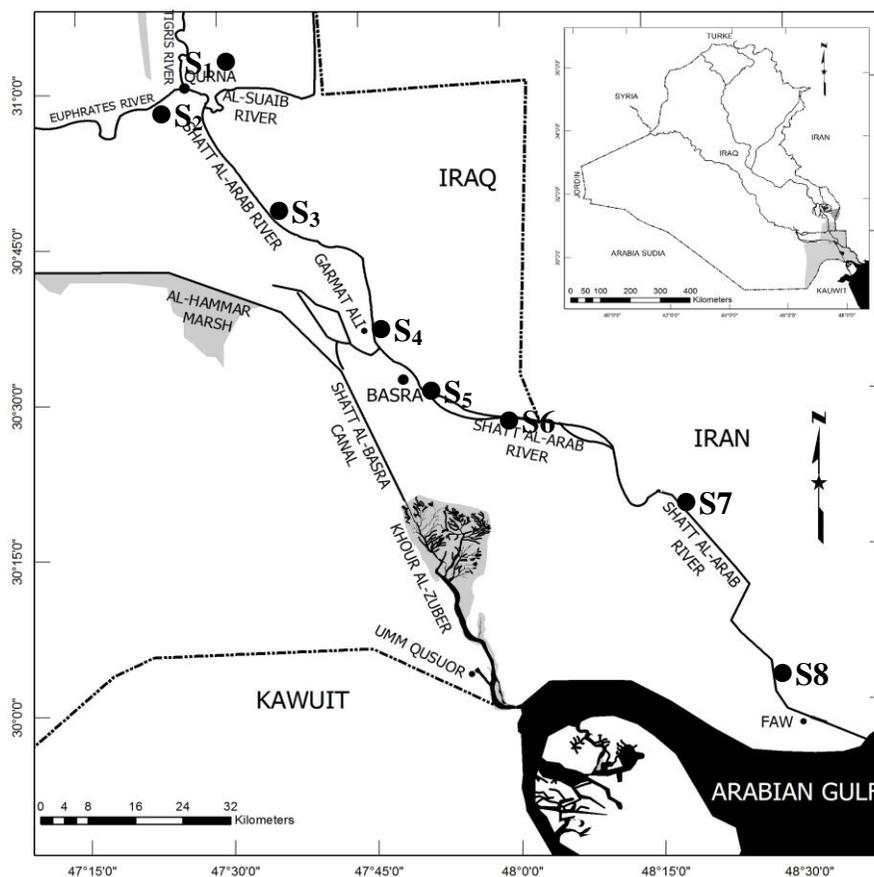


Figure 1. Location map of the study area showing the sampling stations.

Results and Discussion

The following parameters affecting the performance of ammonium determination in natural water by FI system were investigated:

Effect of Sample Volume:

When the manifold in Figure (2) was used, the signal (peak height) of $1.0 \mu\text{gml}^{-1}$ ammonium increased almost parabolic ally with increasing injected sample volume Figure (3) between 20-100 μl therefore, 80 μl was injected in subsequent experimental.

Effect of Carrier Stream flow rate and Total Flow Rate:

The effects of flow rate and total flow rate on peak height of $1.0 \mu\text{gml}^{-1}$ ammonium in the range (0.42-2.0 ml/min) and (1.66-5.2 ml/min), respectively, were shown in Figures 4 and 5. It was found that 1.20 and 3.2 ml/min flow rate for carrier stream and total flow rate were the best, so they are used in subsequent work.

Effect of Mixing and Reaction Coils Length:

The influence of reaction and mixing coils length on peak height of $1.0 \mu\text{gml}^{-1}$ ammonium in the range 20-100 cm and 20-80 cm were studied (Figs 6 and 7). The results show that 60 cm and 50 cm were chosen for reaction and mixing coils length respectively to achieved optimum peak height.

Effect of Nessler reagent:

The greatest peak height was obtained when 12%w/v Nessler reagent. So it was used in subsequent experimental (Fig. 8).

Effect of carrier stream and sodium hydroxide concentrations:

Figures (9 and 10) indicated that peak height increase with increasing of carrier stream and sodium hydroxide concentrations so, 1.0, 1.25N respectively are the best concentrations to be optimized.

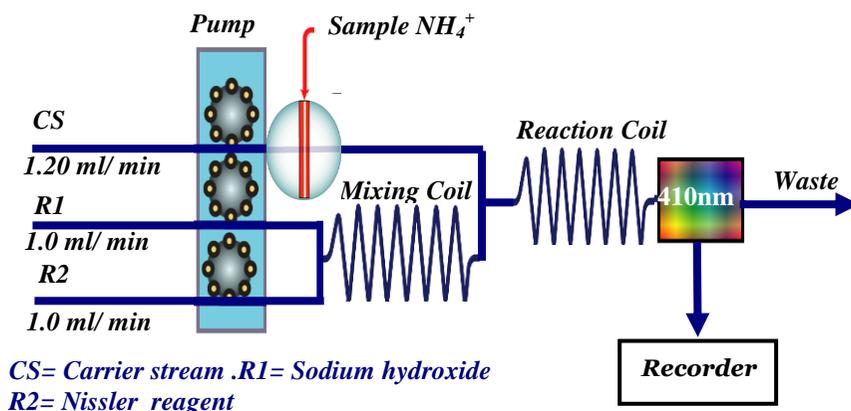


Figure 2. Multi- stream manifold for determination of ammonium.

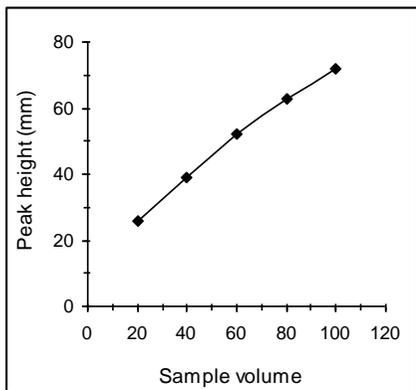


Figure 3. Effect of sample volume.

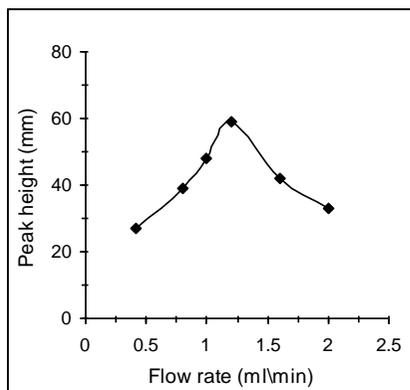


Figure 4. Effect of Flow rate.

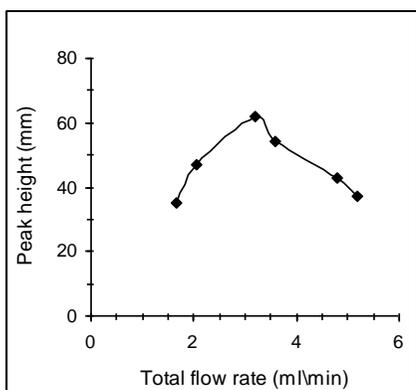


Figure 5. Effect of Total flow rate.

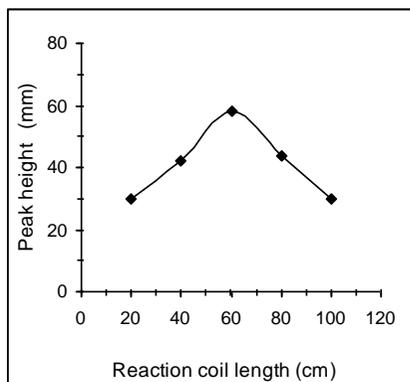


Figure 6. Effect of Reaction coil length.

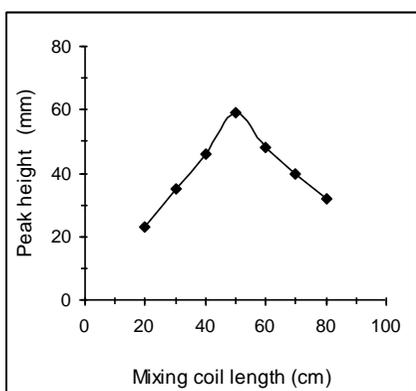


Figure 7. Effect of Mixing coil length

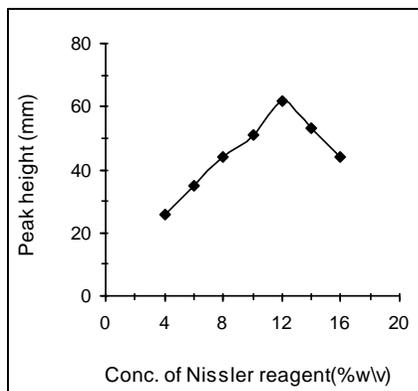


Figure 8. Effect of Nessler reagent concentration

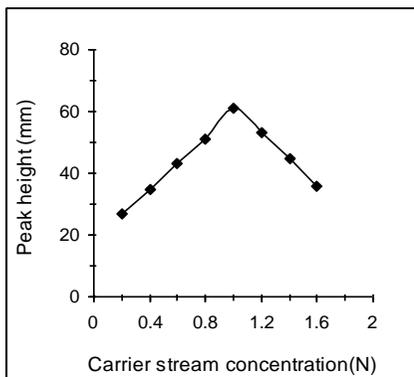


Figure 9. Effect of Carrier stream conc.

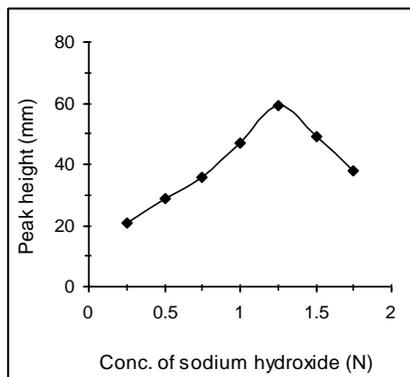


Figure 10. Effect of Sodium hydroxide conc.

Standard Calibration Graph:

Under the established conditions listed in (Table 2), a linear calibration graph for ammonium was obtained over a range 0.25-1.5 $\mu\text{g/ml}$ Figure (11) shows the calibration graph and the recording peak height for series of ammonium standard. The linear graph has a regression coefficient of 0.9998, the detection limit ($2 \times \text{noise}$) was 0.1 $\mu\text{g/ml}$ and the relative standard deviation (R.S.D %) for ten replicates (1.0 $\mu\text{g/ml}$) ammonium was 0.1%, and the sample throughput was 108 sample/h.

Concentrations of Ammonium ion (NH_4^+) in Shatt Al-Arab water:

There are different forms of nitrogen found in water; in this case the form that under study is the ammonium ion (NH_4^+). It is an important analyte for the environmental problem and human health and its detection and quantification is essential (Metcalf, 1991).

Table (3) and Figures (12 - 23) 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 spectrophotometric method. The results indicated that (NH_4^+) concentrations increasing during May, June and July 2010 especially in stations 5 and 6 were (0.95, 1.35), (1.30, 1.25) and (1.45, 1.40 $\mu\text{g/ml}$) 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 (26-34 $^\circ\text{C}$), 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, February 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 $\mu\text{g/ml}$) reported world Health Organization (WHO, 1998).

Table 2. Optimum conditions for ammonium determination by FIA.

Parameters	Value
Sample volume (µl)	80.0
Flow rate (ml\min)	1.20
Total flow rate(ml\min)	3.20
Reaction coil length(cm)	60.0
Mixing coil length(cm)	50.0
Nessler reagent conc. (%w\v)	12.0
Sodium hydroxide conc. (N)	1.25
Carrier stream conc.(N)	1.0

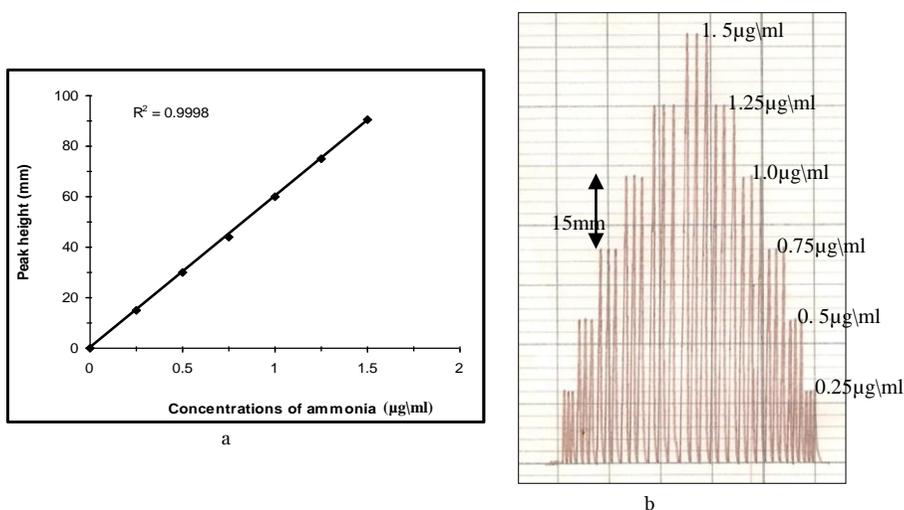


Figure 11 (a). Standard calibration graph for Ammonium determination. (b). Peaks obtained by injected Ammonim Standard.

Table 3. Concentration of ammonium (µg/ml) in different stations during study period.

St.	Concentrations of Ammonium (µg/ml)												Average
	Oct 2009	Nov 2010	Dec 2010	Jan 2010	Feb 2010	Mar 2010	Apr 2010	May 2010	Jun 2010	Jul 2010	Aug 2010	Sep 2010	
1	0.60	0.50	0.25	0.30	0.30	0.40	0.45	0.45	0.65	0.75	0.80	0.65	0.50
2	0.55	0.40	0.25	0.30	0.20	0.35	0.40	0.55	0.60	0.80	0.80	0.60	0.48
3	0.70	0.65	0.25	0.25	0.30	0.30	0.55	0.55	0.60	0.70	0.70	0.30	0.49
4	0.70	0.70	0.40	0.25	0.25	0.50	0.55	0.65	0.70	0.85	1.0	0.90	0.62
5	0.80	0.75	0.35	0.40	0.40	0.65	0.70	0.95	1.30	1.45	1.35	1.20	0.85
6	0.85	0.75	0.40	0.40	0.50	0.60	0.65	1.35	1.25	1.40	0.95	0.90	0.83
7	0.55	0.55	0.35	0.30	0.35	0.35	0.35	0.55	0.43	0.75	0.60	0.50	0.47
8	0.40	0.45	0.25	0.20	0.30	0.30	0.30	0.30	0.30	0.35	0.40	0.25	0.31

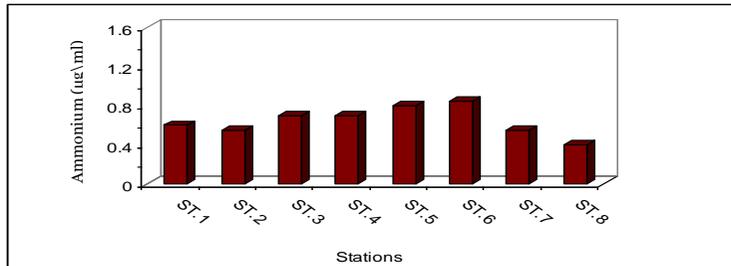


Figure 12. Variations of ammonium concentrations in the study area (Oct. 2009).

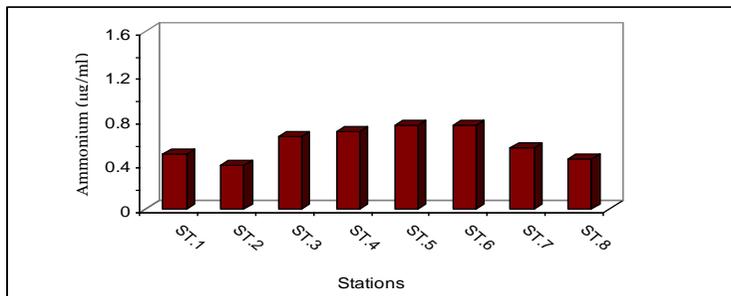


Figure 13. Variations of ammonium concentrations in the study area (Nov. 2009).

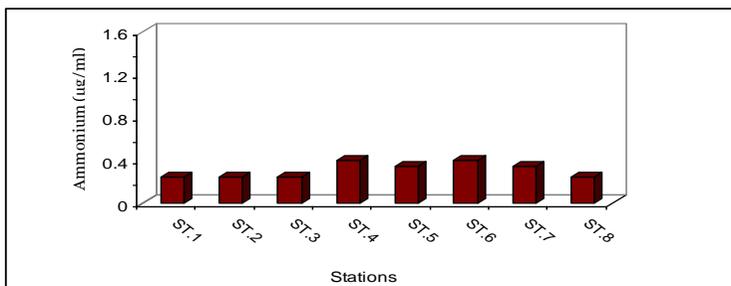


Figure 14. Variations of ammonium concentrations in the study area (Dec. 2009).

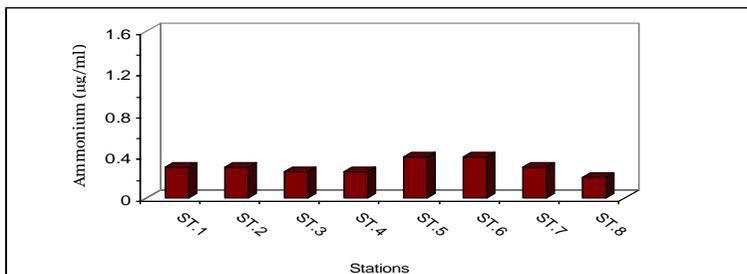


Figure 15. Variations of ammonium concentrations in the study area (Jan. 2010).

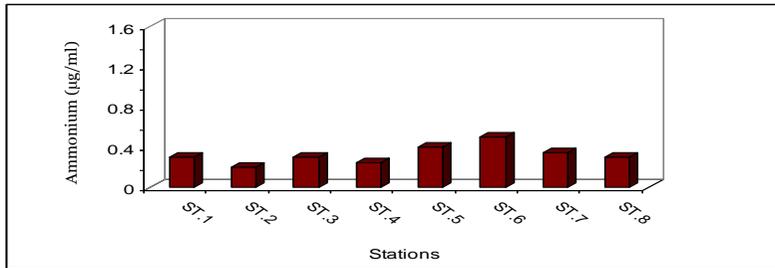


Figure 16. Variations of ammonium concentrations in the study area (Feb. 2010).

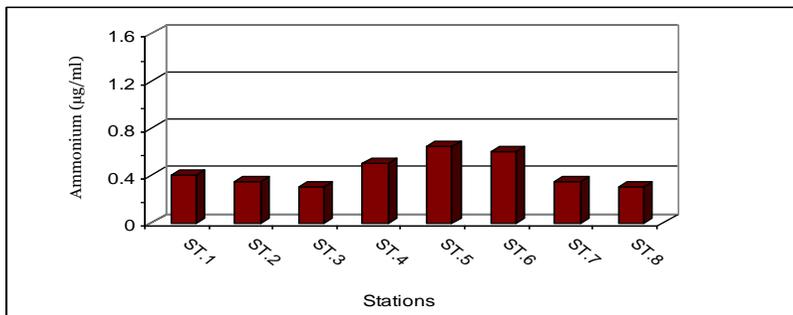


Figure 17. Variations of ammonium concentrations in the study area (Mar. 2010).

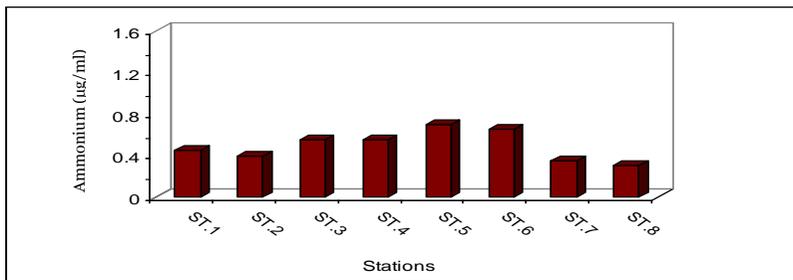


Figure 18. Variations of ammonium concentrations in the study area (April 2010).

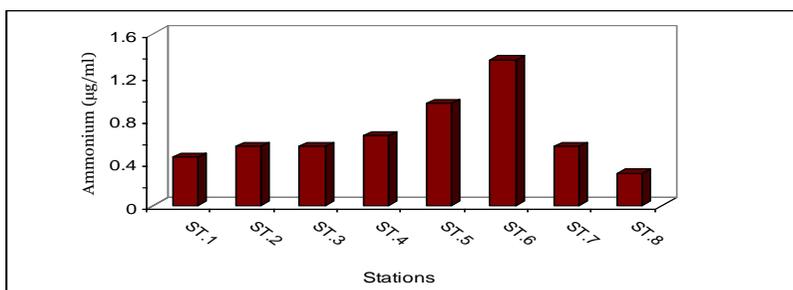


Figure 19. Variations of ammonium concentrations in the study area (May 2010).

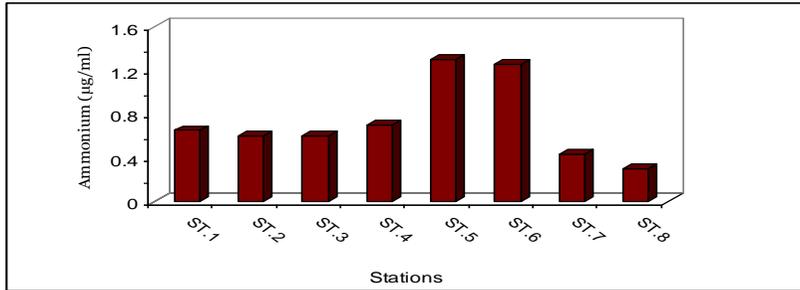


Figure 20. Variations of ammonium concentrations in the study area (June 2010).

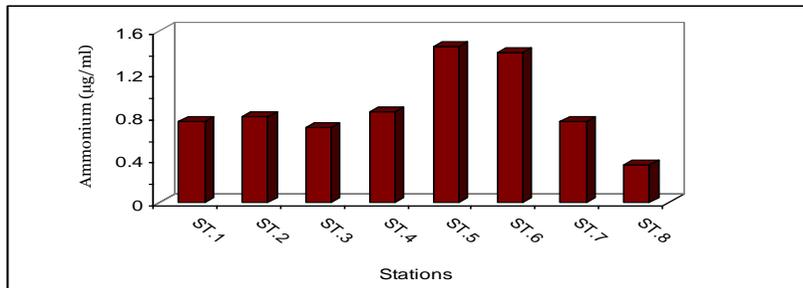


Figure 21. Variations of ammonium concentrations in the study area (July 2010).

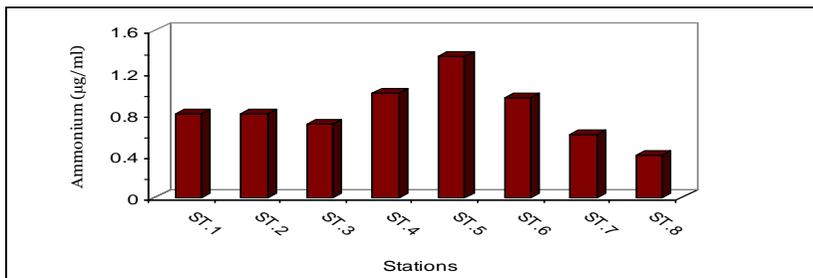


Figure 22. Variations of ammonium concentrations in the study area (Aug. 2010).

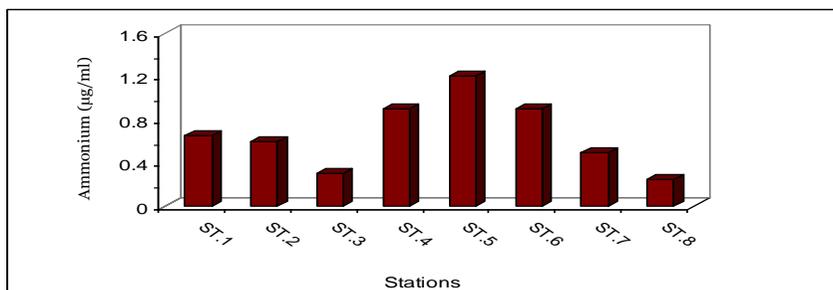


Figure 23. Variations of ammonium concentrations in the study area (Sept. 2010).

Conclusion

A home-made semi-automated FI spectrophotometric provides simple, fast, reproducible and sensitive method for the determination of ammonium levels in water of Shatt Al-Arab water. The recorded levels of ammonium in the study area are higher than reported previously, but still the area is not polluted with ammonium.

References

- APHA (American public health association standard method for the examination water and wastewater) 1999. 20th ed, New York, USA.
- Al-Maliki, A.D.M. 2001. Levels of ammonia in some branches of Shatt Al-Arab river. *Marina Mesopotamica*, 16(2): 539 – 549.
- Barnett, N.W., Lenhan, C.E. and Lewis, S.W. 1999. Sequential injection analysis: an alternative approach to process analytical chemistry. *Trends Anal. chem*, 18(5): 353 – 364.
- Douabul, A.A.Z., Abaychi, J.K., Al-Asadi, M.K. and Al-Awadi, H. 1987. Restoration of heavy polluted branches of the shaft al-Arab river, Iraq. *Wat. Res.*, 21(8): 955 – 960.
- Gibbs, S.W., Mantoura, R.F.C. and Liss, P.S. 1995. Analysis of ammonia and methylamines in natural waters by flow injection gas diffusion coupled to ion chromatography. *Anal. Chem. Acta.*, 316: 291 – 304.
- Jeffrey, S.L. 1995. *Marine Biology*. Oxford University press, INC.
- Joaquim, A.N. and Antonio, A.M. 1995. A Flow injection spectrophotometric determination of ammonium in natural water. *J. Braz. Chem. Soc*, 6(4): 327 – 330.
- Miller, G. and Tyler, Jr. 2002. *Living in the Environment*, 12th ed, Belmont: Wadsworth Thoomson Learning. ISBN.
- Metcalf, E. 1991. *Wastewater Engineering, Treatment, Disposal and Reuse*. McGraw-Hill.
- Maulood, B.K., Hinton, G.C.F., Whitton, B.A. and Al-Asadi, H.A. 1981. On the algal ecology of the lowland Iraqi marshes. *Hydrobiologia*, 80: 269 – 276.
- Quinn, P.K. 1996. Estimation of the air/sea exchange of ammonia for the North Atlantic basin *Biogeochemistry*, 35: 275 – 283.
- Roslyn, J.W., Edward, C.V., Butler, L.C. and Kate, M.B. 2004. Flow injection analysis with fluorescence detection for the determination of trace levels of ammonium in sea water. *J. Environ. Monit.*, 7: 37 – 42.
- Ruzicka, J. and Hanses, E.H. 2005. *Flow injection analysis*. 3rd ed., J. wily New York.
- Saad, M.A.H. and Kell, V. 1975. Observations on some environmental conditions as wel as Plankton blooms in the lower reaches of Tigris and Euphrates. *Wissenschaftliche Zeitschrift Der Universitat Rostock. Mathematisch Naturwissenschaftliche*, 24: 781 – 788.
- Trojanowicz, M. 2008. *Advances in Flow Analysis*, wily-VCH.verlag-GmbH and CO.KGA.Wanhheim, 672p.
- Wetzel, R.G. 1983. *Limnology*. 2nd ed. Saunders college publishing. Philadelphia, USA, 858p.

بناء وحدة تحليل حقن جرياني لتقدير أيون الأمونيوم في مياه شط العرب

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المستخلص - تم بناء وحدة تحليل حقن جرياني شبه ذاتية لتقدير أيون الأمونيوم في عينات مياه شط العرب شهرياً للفترة من تشرين الأول 2009 لغاية أيلول 2010 في ثمان محطات [القرنة (دجلة)، القرنة (الفرات)، جسر سعد، گرمة علي، العشار، أبو الخصيب، السببة والفاو] تشير النتائج الى زيادة في تراكيز أيون الأمونيوم خلال أشهر مايس، حزيران وتموز 2010 وخصوصاً في المحطات 5 و 6 وكالاتي (0.95, 1.35)، (1.30, 1.25) و (1.40, 1.45) مايكروغرام/مل وعلى التوالي. أن وحدة تحليل الحقن الجرياني لتقدير أيون الأمونيوم طبقت بنجاح ووفرت هذه الطريقة بسيطة وسريعة وأستعادية.