

Determination of phosphate levels in the southern part of Al-Hammar marsh water by flow injection analysis

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Abstract - Flow Injection Analysis (FIA) was applied to determine phosphate concentration in water of the southern part of Al-Hammar marsh water from July 2007 to July 2008. A linear line was obtained over the range 0.25- 1.75 µg/ml of phosphate with regression coefficient for seven points is 0.9999. The detection limit was 0.075 µg/ml with % R.S.D for ten replicate analysis of 1.0 µg/ml phosphate is 0.511% and the dispersion coefficient in the flow system is 5.4. The samples can be analyzed at rates exceeding 72 sample per hour .It was noted that phosphate concentration ranged 0.295 - 1.450 µg/ml, whereas the maximum phosphate concentration was recorded in spring 2008 and the minimum in autumn 2008.

Key words: Flow injection analysis, Phosphate, Nutrients, Spectrophotometer.

Introduction

The pollution with phosphate has become a major environmental problem. The reasons for this was markedly increased the use of commercial cleaning with phosphate were widely used as detergent. Phosphate, also enter the water supply from agriculture fertilizer, run off water treatment and biological water and residues (Nollet, 2007).

Flow injection analysis (FIA) is a major methodological innovation characterized by its simplicity, relatively inexpensive equipment handily operated and great capacity for achieving results that are excellent in view of the rapidity, accuracy and precision with which they are obtained. The extreme versality of this technique makes it stand out from most new analytical techniques (Ruzicka and Hansen, 2005). The present interest in pollution monitoring has resulted in the development of new analytical method or the a daption of existing methods for determination of pollution .In view of the growing demand for such analysis, the analytical method developed for the purpose should be operated on a continuous basis (Trojanowicz 2008). In fact this is one of the areas where FIA is most frequently applied (Ruzicka and Hansen, 2005).

Various FIA methods have been proposed for the determination of phosphate (APHA, 1999). Among thes are the spectrophotometric determination of phosphate by FIA which was applied for the determination of phosphate in southern area of Hor al-Hammar by a home- made semi-automated FIA system.

Materials and Methods

All reagents used were analytical (grade) unless otherwise stated and all stock and standard solutions were prepared in pure deionized distilled water.

Reagents and Solutions:

Phosphate standard solution (100 $\mu\text{g ml}^{-1}$):

Potassium dihydrogen phosphate KH_2PO_4 is dried in an oven at 110°C then in a desiccator. Exactly 0.1432g was dissolved in 1L of deionized distilled water. Phosphate standard over the rang 0.25 -1.75 $\mu\text{g ml}^{-1}$ were prepared by serial dilution in distilled water.

Ascorbic acid (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 ($6 \times 10^{-3} \text{ M}$):

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.

Sampling and storage:

The representative water sample were collected in clean chemically resistant plastic bottle from eight stations in the southern part of Al-Hammar marsh as shown in Figure (1).

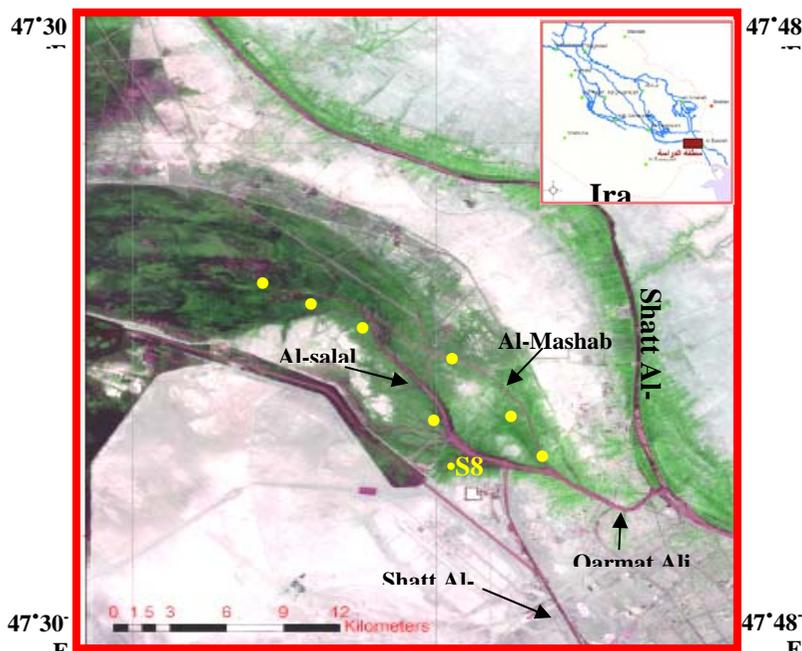


Figure 1. Map of South Iraq showing study area.

The water samples were taken from 30cm down the water surface. The samples were filtered by 0.45 μm membrane filter (GF/C Whatman Germany) which was rinsed for 24h in 2L of water and then washed for many times by deionized distilled water to be phosphorus-free (APHA, 1999). Two drops of chloroform were added to the filtered sample before storage in freezing (APHA, 1999).

Instrumentation:

All flow injection measurements were made by using a home-made semi-automated FIA system as shown in Fig.2 which was previously described (Al-Jorany, 2008).



(a)



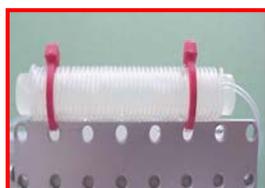
(b)



(c)



(d)



(e)



(f)



(g)

Figure 2. (a) Home made semi-automated flow injection system, (b) Injection valve, (c) Spectrophotometer, (d) Recorder, (e) Teflon reaction, (f) Flow cell, (g) Peristaltic pump.

Procedure:

The carrier stream was deionized distilled water run into the manifold Fig.3 at flow rate 0.73 ml/min. 90 μ l as a sample volume of phosphate was injected manually through injection valve into the carrier stream. The ammonium molybdate and ascorbic acid solutions were pumped at equal flow rate 0.95 ml/min for each of them. The two solutions are mixed by 40 cm mixing coil and then the mixed solution merge with carrier stream, so the reaction between phosphate and the reagent take place at 50 cm reaction coil. The absorbance of the formed complex was measured at 660 nm by spectrophotometer equipped with flow cell. The mean of triplicate peaks heights can be related to the sample concentration.

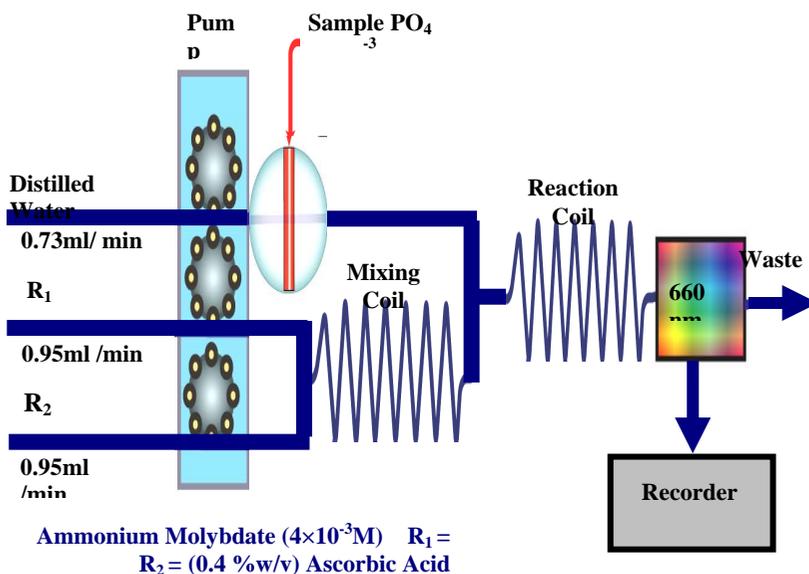


Figure 3. Multi-stream manifold for determination of phosphate.

Results and discussion

The home-made semi-automated FI system as shown in Fig.2 was used to optimize the variables by conducting a series of experiments to establish the optimum analytical conditions that influence the peak height were investigated:

1. Effect of Sample Volume

The effect of sample volume on the peak height of $1.0 \mu\text{g ml}^{-1}$ phosphate is shown in Fig.4. The maximum peak height was obtained with injection of 90 μ l, therefore 90 μ l was used to inject in subsequent work to obtained good sensitivity because the dispersion of the formed complex decrease with increasing of sample volume (Christian, 2003).

2. Effect of Mixing and Reaction Coils Length

Effect of increasing various length of mixing and reaction coils of tubing into the manifold are shown in (Fig. 5 and 6). The results showed that increasing the coils length more than 40 cm and 50 cm for mixing and reaction coils respectively leads to more dispersion in the flow system. So, 40 cm and 50 cm were chosen for subsequent work for mixing and reaction coils respectively.

3. Effect of Carrier Stream flow rate and Total Flow Rate.

(Fig. 7 and 8) shows the effect of carrier stream of flow rate and total flow rate on the peak height of $1.0 \mu\text{g ml}^{-1}$ phosphate. The reaction between phosphate and the reagent was found to be instant when stopped flow method was used. The results are indicated that the peak height decrease with increasing the flow rate (Ruzicka, 2005). This was thought to be due to increasing of dispersion of the formed complex with the increasing the flow rate. A 0.73 ml/min and 2.63 ml/min were chosen for carrier stream and total flow rate respectively.

4. Effect of Ascorbic Acid Concentration

The influence of ascorbic acid concentration on the peak height for $90 \mu\text{l}$ of $1.0 \mu\text{g ml}^{-1}$ phosphate is shown in Fig. (9). The peak height increases with increasing the concentration of ascorbic acid, which thought to be due to more complex formed. The peak height decreased above 0.4% (w/v) ascorbic acid, so this concentration was used in subsequent experiments.

5- Effect of Ammonium Molybdate Concentration

The influence of ammonium molybdate concentration on the peak height for $90 \mu\text{l}$ of $1.0 \mu\text{g ml}^{-1}$ phosphate is shown in Fig. (10). The peak height increases with increasing the concentration of ammonium molybdate which thought to be due to more complex formation, above $4 \times 10^{-3} \text{ M}$ the peak height was decrease. Thus $4 \times 10^{-3} \text{ M}$ ammonium molybdate was used subsequent experiments.

Standard calibration graph:

Under the established conditions (Table1) a calibration graph for phosphate determination was obtained (Fig. 11 and Table 2) it is linear over a range of $0.25 - 1.75 \mu\text{g ml}^{-1}$. The linear graph has a regression coefficient of 0.9999 (five points). The relative standard deviation for ten replicates was $\pm 0.511\%$ and the detection limit ($2 \times \text{noise}$) was $0.075 \mu\text{g ml}^{-1}$. The dispersion in the flow system was 5.4 and the sample throughput could be up to 72 sample/h.

Study of Interference:

Aluminum and silicate are known to interfere seriously with the spectrophotometric method of phosphate determination, but most common metals have no effect (Al-Maliki, 1999). Therefore only the effect of Al^{+3} and SiO_2^{-2} were measured by adding 10, 100, and 1000 folds of each ions to $1.0 \mu\text{g ml}^{-1}$ phosphate.

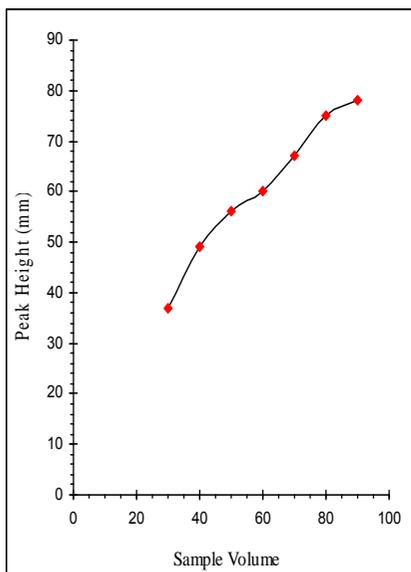


Figure 4. Effect of Sample

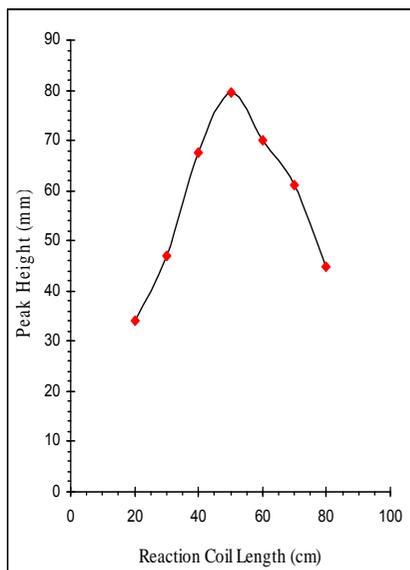


Figure 5. Effect of Reaction

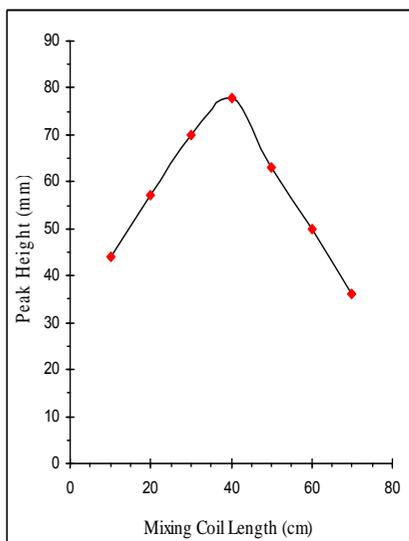


Fig.6. Effect of Mixing Coil

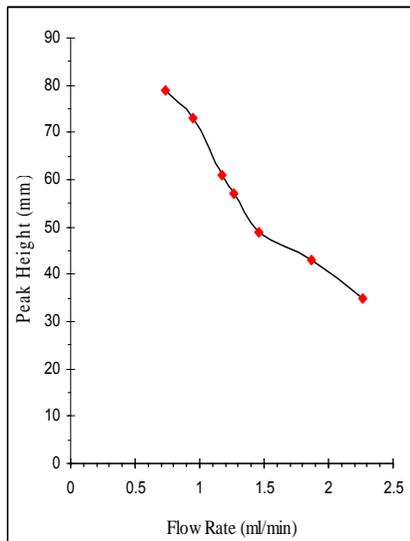


Fig.7. Effect of Flow Rate

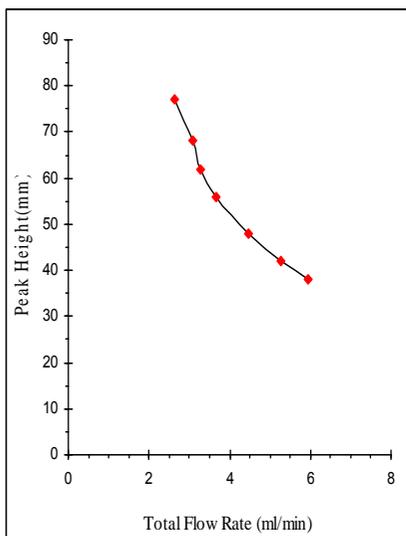


Figure 8. Effect of Total

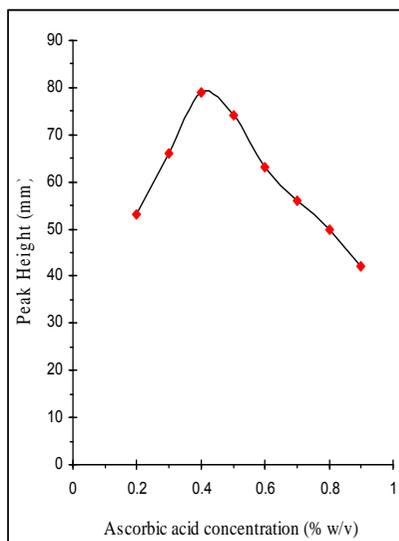


Figure 9. Effect of Ascorbic acid

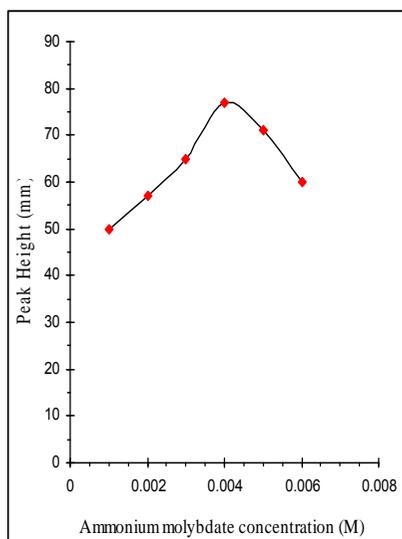
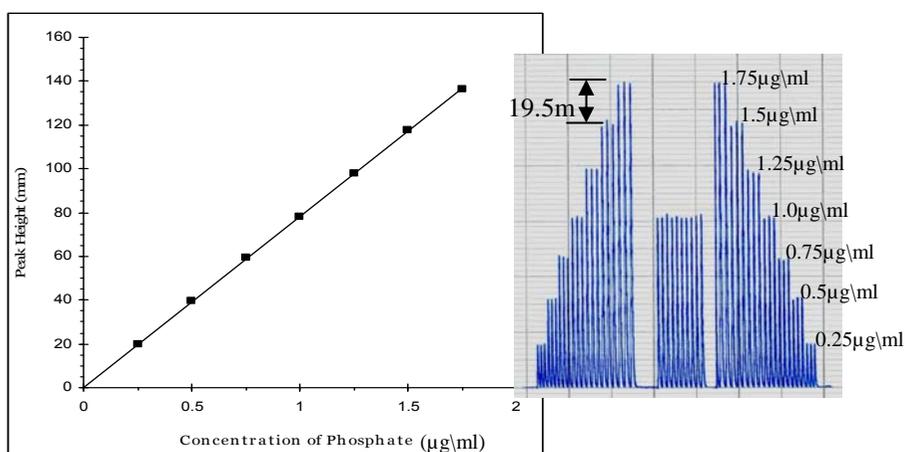


Fig.10.Effect of Ammonium Molybdate

Table 1. The Optimum Conditions for FI Phosphate determination.

| Parameters | Value |
|----------------------------------|----------------------|
| Sample Volume | 90 μl |
| Reaction Coil Length | 50 cm |
| Mixing Coil Length | 40 cm |
| Carrier Stream Flow Rate | 0.73 ml/min |
| Total Flow Rate | 2.63 ml/min |
| Ascorbic Acid Concentration | 0.4% (w/v) |
| Ammonium Molybdate Concentration | 4×10^{-3} M |

Figure 11. (a) Corresponding calibration graph of phosphate, (b) peaks obtained by injected phosphate, (c) 10 replicates of 1.0 $\mu\text{g/ml}$ standard phosphate.Table 2. Standard calibration graph of 1.0 $\mu\text{g ml}^{-1}$ phosphate.

| Conc. of Phosphate ($\mu\text{g ml}^{-1}$) | Peak Height (mm) | R.S.D % |
|--|------------------|---------|
| 0.25 | 19.75 | 0.0169 |
| 0.5 | 39.5 | 0.253 |
| 0.75 | 58.5 | 0.437 |
| 1.0 | 78.0 | 0.0746 |
| 1.25 | 97.5 | 0.0136 |
| 1.5 | 117.0 | 0.425 |
| 1.75 | 136.5 | 0.0733 |

Al^{+3} decrease the peak height due to forming un-dissolved complex (Cotton 1980). This effect can be eliminated by incorporating a mini-column of strong ion – exchange to remove all cations in the sample (Al-Mousawi, 2009). Also this is not a serious problem for Al^{+3} and SiO_2^{-2} because the tolerable concentration is greater than commonly encountered in the study area (Adum *et al.*, 2007). Silicate is clearly enhancing the peak height of $1.0 \mu\text{g ml}^{-1}$ because the silicates also react with the same reagent which is used for phosphate determination and form a blue complex (Al-Jorany 2008). This effect can be rendered harmless by adding tartaric acid or oxalic acid which is already used in the determination of silicate to destroy the formed complex between phosphate and the completing reagents (Thomsen *et al.*, 1983).

Discussion

Figure 12 showed the phosphate concentrations in the study area during the period from July 2007 to July 2008 which were obtained by the semi-automated FIA spectrophotometric method.

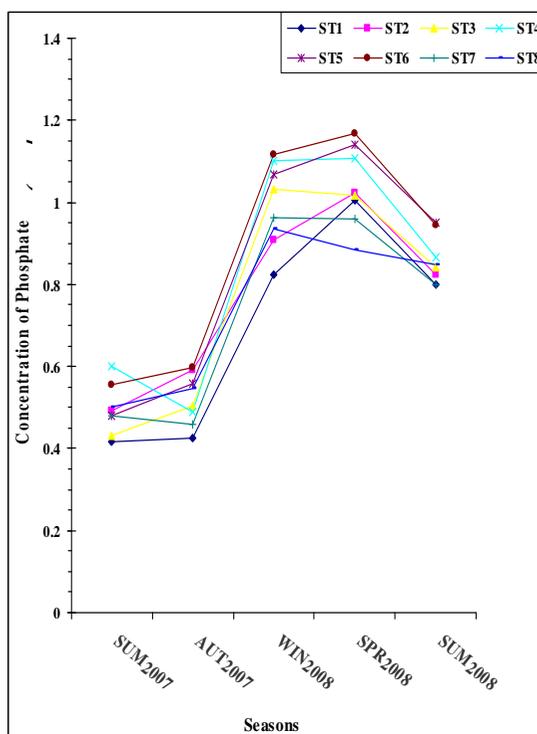


Figure 12. Seasonal variation of phosphate concentrations.

The results clearly indicated that phosphate concentrations increasing during this period of study and reached its maximum at spring 2008. It is worth notice that phosphate concentrations in all stations and especially in stations 4,5, and 6 higher than previously reported by other workers in the study. (Al-Imarah *et al.*, 2006 ; Al-Sowdani *et al.*, 1991). They also reported that the maximum phosphate concentration during the seasonal variation at winter. These results may be thought due to many reasons: Firstly, the year of 2008 can be classified as a dry year due to quantity of rain. Also, the rain fall during spring in the study period may cause agricultural fertilizer run-off into the water suppliers in the study area.

Secondly, due to deuration of water quality in the study area during this period which it is worth notice the electrical conductivity of the water increased from 3.125 to 7.78 ms/cm in July 2007 to July 2008 respectively. The high salinity of water may lead to increase of phosphate concentration due to librate phosphate absorbed on the small practical size of sediments to the water (Al-Abaychi, 1988). Finally, the level of phosphate water general and especially in the study area is not polluted with phosphate comparing with World health organization (WHO) and (united state environmental protection agency (USEPA)).

Conclusion

A home-made semi-automated FI spectrophotometric provides simple, fast, reproducible and sensitive mean of determination of phosphate levels determination in water of southern part of Al-Hammar marsh. The recorded levels of phosphate in the study area are higher than reported previously, but still the area not polluted with phosphate.

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قياس مستويات الفوسفات في مياه الجزء الجنوبي لهور الحمّار بتحليل الحقن الجرياني

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المستخلص تم تطبيق تقنية الحقن الجرياني (FI) لتقدير الفوسفات في مياه الجزء الجنوبي لهور الحمّار للفترة من تموز- 2007 ولغاية تموز- 2008. وكانت العلاقة الخطية ضمن المدى 0.25 -1.75 µg/ml بمعامل ارتباط 0.9999 وأن حد الكشف (noise×2) 0.075 µg/ml ومعامل الانحراف القياسي النسبي %r.s.d لعشر قراءات من 1.0 µg/ml فوسفات يساوي %0.511 وكان معامل التخفيف لنظام الجريان 5.4 وأن سرعة النمذجة 72 sample/h وتراوحت تراكيز الفوسفات بين 0.295- 1.450 µg/ml لمناطق الدراسة المختلفة . وسجلت أعلى القيم خلال فصل الربيع 2008 وأقلها خلال فصل الخريف 2008.