Available online at: http://brsj.cepsbasra.edu.iq

2695 -1817 -ISSN

Applications Of Home -Build Micro Flow Injection (µFIA) Spectrophotometric system for Chloride Determination in Water

YOUSIF SHAFI J. ALJORANI [1] AND K. H. AL-SOWDANI [2]

1Applied marine sciences department- Faculty of marine sciences- Basrah University/IRAQ

2 Chemistry department-colleges of education and pure science- Basrah University/IRAQ

Corresponding author: E-mail: yousif.shafi@yahoo.com

Abstract

A home-build micro flow injection analysis (µFIA) was constructed and used for chloride ion detection in natural and freshwater samples which were collected from Shatt al-Arab river and the Basrah city- south of Iraq. Two labs- made microcontroller software programs were designed .The first program, type UNO used to control the lab- made mini peristaltic pump to propel the chemicals reagents to detector. While, the other program was Mega type which was employed as a data-logger to manipulate and recording the response as peak height corresponding the concentration by using Microsoft Excel 2010 program. The linearity, regression coefficient for seven points, detection limit and %R.S.D for ten replicates of 25 µg/ml were 5-35 µg/ml, 0.9984, 0.5 µg/ml and 0.0597 % respectively. The sample throughput was 120 samples per hour. so each one sample consumed 94.2µL of chemical reagents and 120 samples consumed 11.30ml of chemical reagents. The home build semi-automated micro-flow injection analysis (µFIA) system was applied successfully for chloride estimation with simple manifold, high sensitive and accurate.

Keywords: micro flow injection, chloride, Spectrophotometric, Natural water.

1. Introduction

Flow injection analysis (FIA) is one of analytical methods based on injection of the sample into the carrier stream which propel it to the detector [1] The concept of flow injection (FI) was introduced in pioneering paper by Ruzicka and Hansen in 1975 [2], through inject a small volume of analyte into a carrier stream moving in a tube having micro diameters to a detector where the results is recorded as peak height, This is called conventional or normal flow injection [3, 4]. The other form was introduced by Johnson and Petty [5] named reverse flow injection where the reagent is injected in the sample solution. In addition, there are other various forms of flow injection analysis included merging zone, split-loop injection, stopped flow and gas diffusion [6, 7]. FIA has many applications in many aspects like biological, chemical, clinical, drugs, industrial, food and environmental analysis [8-11].It has been described for some aspects as diluting and transported the sample automatically in a various flow systems to eliminate interference in the measurement step and reducing reagents, samples consumption to micro liters.[12,13].Micro flow injection system is

now used in chemical ,biological, pharmaceutical analysis and other fields because low reagent consumption, miniaturizing the sample, waste storage, simple procedure in addition to high speed, precision and accuracy [14,15]. Minimizing the flow analysis system can be achieved by constructing manifolds with diminutive detectors and transporting the carrier stream with large hydraulic device [16, 17]. Micro syringes and micro controlling pump to displacement the peristaltic pumps [18, 19] and micro tubes was used in all parts of the manifold. These lead to miniaturized the flow injection apparatus with micro diameters tube [4] Chloride detection based on mercury thiocyanate method by Utsumi et al, this method used mercury thiocyanate and ferric as reagents and is based on the reaction of thiocyanate ion with chloride then the liberated thiocyanate react with iron (III), to product a reddish - orange iron (III) - thiocyanate complex. The intensity of the iron (III) -thiocyanate complex is calculated at specific wavelength spectrophotometrically and the concentration of chloride is measured from the corresponding intensity of the complex color Several techniques were reported for chloride evaluation like, gravimetric method, the volumetric Volhard and Mohr methods, spectrophotometric methods, Turbidimetric and mercurometric method [20-22].Spectrophotometric determination of chloride was reported by a few workers in Iraq [23].The reagent used is toxic, since it contains mercury, since µFIA generates much smaller amounts of waste than manual procedures.

2. Experimental

2.1. Chemicals:

Analytical grade reagents and deionized water were used through this work. All samples were analyzed in triplicate and the absorbance of corresponding blank was subtracted. The solution for chloride detection was prepared by dissolve 0.208g mercuric thiocyanate, 10 g ferric nitrate Fe $(NO_3)_3 \cdot 9H_2O$ and 10 ml of concentrated nitric acid then mixed and diluted to 1L. Chloride standard solution (1000 µg/ml) was prepared by dissolving 1.648g sodium chloride in 1L water. Chloride standard over the rang 5.0-35 µg/ml were prepared by serial dilution in water.

2.2. Micro flow injection manifold

Home build (µFIA) system was shown in Fig.1. It used for chloride determination in water samples. It is consist a two microcontrollers UNO and MEGA types. These two microcontrollers were provided with build home software programs. The first program, type UNO used to control home- build peristaltic pump with variable speed in the rang 0.4-5 ml/min to drive reagents to detector. The second was MEGA type which was used as data-logger to manipulate and recording the response as peaks height corresponding the concentration by using Microsoft Excel 2010 program. Sample Cl^- 20µL was injected through injection valve supplied with variable loops 15-35 µL. The reaction coil was made from 0.2 mm i.d tube (supplied from Technicon Instruments corporation) in order to minimize consumption of reagents. Detector was spectrophotometer (SPECTRO SC, Labomed, Inc,USA) which supplied with 7 µL flow cell (QS Hellma).

3. Results and discussion

3.1. Method optimization

To achieve high sensitivity, linear calibration range and economy of reagent consumption, the effect of various physical and chemical parameters were examined. All of these studies were performed with a chloride standard solution 25 µg/ml and were carried out in triplicate. Flow rates for one channel were examined over the range 0.6 – 1.5 ml/ min as illustrated in Fig.2, the peak height decreased with increasing the flow rate. This was thought to be due to increase of the dispersion with increasing flow rate because of the instant complex formation therefor, a 1.0 ml/min flow rate was chosen for subsequent work [4,6]. Sample volume was also evaluated over the range 15 – 35 µL , the absorbance and peak height maximum increased gradually with sample volume, but a 20 µL volume gave the best shaped peaks, good sensitivity and high sample throughput as shown in Fig.3. [4, 6] Finally, the influence of Reaction coil length on peak height of 25 µg/ml chloride was shown in Fig 4.The results indicated the increasing of the reaction coil length leads to increase peak height [24] therefor, a 30 cm was chosen .Table (1) summarized the optimum conditions for chloride determination by micro flow injection system.

Table 1: The optimum conditions for µFIA

parameters	values
Internal diameter of tubes (I.D)	0.2 mm (i.d)
Total flow rate	1.0 ml/min
Sample volume	20µL
Reaction coil length	30cm

3.2. Spectral features

The spectral scans of Iron (III) – Thiocyanate complex was determined under the established condition over the range 200-800 nm as shown in Fig 5. Maximum wavelength of 480 nm was chosen for following work in the proposed system.

3.3. Standard Calibration Curve

On the proposed µFI system, the calibration graph was detected by using the working standard solutions of chloride ion over the concentration range 5 to 35 µg/ml as shown in (Fig. 6 and table 2.) RSD% for ten injections was 0.0597% of 25 µg/ml of chloride ion and the detection limit was 0.5 µg/ml of chloride ion. The equation y=2.9714 give the relationship between the peak height and the concentration where y and x were the peak height and the concentration of Cl^- respectively; The Regression coefficient was 0.9984 for seven points . The dispersion coefficient in flow system was 1.55 as shown in Fig 7. The sample throughput was 120 samples /h, so each one sample consumed 94.2µL of chemical reagents therefore, 120 samples consumed 11.30 ml of chemical reagents.

Table 2 Standard Calibration graph of standard chloride ion

Chloride conc. (µg/ml)	Peak height (mm)	(r.s.d %) (3 replicates)
5	15	0.0123
10	28	0.0233
15	44	0.0369
20	62	0.0206
25	76	0.0558
30	88	0.0285
35	103	0.0434

3.4. Interferences study

Bromide and Iodide are known to interfere seriously with the spectrophotometric method of chloride determination by mercuric thiocyanate method, but most common ions have no effect. Carbonate and sulfide interference was neglected by acidification of the solution by nitric acid. Therefore the effect of Br^- and I^- and some ions were measured by adding 25, 50, and 100 µg/ml of each ions to 25 µg/ ml chloride. The peak height obtained was compared with the peak height of non-interfering ions. Bromide and Iodide gave a serious enhancement of the peak height (Table 3, Fig 8) Because of high sensitivity of the method interfering substance can rendered harmless by dilution. Also this not a concentration is greater than commonly encountered in. The concentrations of bromide and iodide in Shatt Al-Arab River were 0.19 and 0.61 µg/ml respectively.

Table 3: Interferences effect on determination of chloride

Add ion Conc. µg/ml	Peak height (mm)							
	Ca^{+2}	Mg^{+2}	Na+	K^+	NO_3^-	NO_2^-	I^-	Br^-
25	76	74	75	76	73	75	53	56
50	75	75	74	76	74.5	76	46	48
100	75	74	74	74	75	76	35	33

3.5.Analytical application

Different samples of water were collected from shatt al-Arab River and different sites of fresh water in Basrah city south of Iraq in summer 2019. The concentrations of chloride in the sample were measured spectrophotometrically at 480 nm by µFIA system. The accuracy test was carried out by matching the results of our lab. Made system with Mohr classical methods as shown in table 4 .Additionally, the micro flow injection method is simple, inexpensive, rapid, and has a high sensitivity. and consume a small amounts of samples and reagents

Table 4: Concentrations of chloride in natural and freshwater by µnFIA

Sample No.	Sample	Concentrations of chloride (µg/ml)	
		rµFIA ± r.s.d	Classical method± r.s.d
1	Al-Qurna /Euphrates river	700±0.0265	710±0.0963
2	Al-Qurna/Tigris river	700±0.0216	785±0.152
3	Khour al-zubair	6300±0.0311	6620±0.0895
4	Al-sharsh/ Shatt al-Arab river	650±0.0287	610±0.0843
5	Al-deer/ Shatt al-Arab river	575±0.0522	620±0.198
6	Saad bridge/ Shatt al-Arab river	525±0.0433	600±0.162
7	Qurmat ali river	850±0.0489	780±0.176
8	Ashar/ Shatt al-Arab river	750±0.0255	840±0.0976
9	Abu al-Khasib/ Shatt al-Arab river	1000±0.490	910±0.165
10	Fao/ Shatt al-Arab river	2550±0.0256	2470±0.0932
11	Messan/Tigris river	400±0.0273	440±0.0058
12	Al-geraf river/Nasiriya	300±0.0177	390±0.764
13	Fresh water/Al-khalij quarter	200±0.0136	-
14	Fresh water/AL-asdeqa quarter	225±0.0281	-
15	Fresh water/Al-hussain quarter	200±0.0498	-
16	Fresh water/ Qurmat ali quarter	250±0.0133	-
17	Fresh water/ Al-twisa quarter	225±0.0311	-
18	Fresh water/ al-zubair	150±0.375	-
19	Ground water/ al-zubair	3100±0.0360	3260±0.345

References

[1] C.Victor, F.Laura and C.Amalia Flow analysis: A Practical Guide, Elsevier, Amsterdam-Netherlands, (2014)

[2] SD.Kolev and ID.Mckelvie, Advances in flow injection analysis and relate techniques. 1st ed. United Kingdom: Elsevier Science; (2008).

[3] A.Pharik, K.Patel and C. Patel C and BN. Patel, ***J Chem. Pharm. Res***., 2 (2) 118, (2010).

[4] J.Ruzicka and E.H.Hansen, Flow Injection Analysis.3rd Ed., J.wily, New York, (2005).

[5] K.S. Johnson, R.L. Petty, ***Anal. Chem***. 54, 1185 (1982).

[6] M. Trojanowicz Advances in Flow Analysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2008.

[7] M. Trojanowicz. ***Mod. Chem. Appl***., (3), 1, 2013.

[8] D., Michel, M., Casey Gaunt, T., Arnason, A.,El-Aneed . ***J Pharm Biomed Anal***, 107, 299,(2015).

[9] Zhao C, Shao C, Li M, Jiao K. ***Talanta***, 71, 1769, (2007)

[10] M. Knochen and J. Giglio, ***J. Pharm. Biomed. Anal***. 33, 191, (2003)

[11] JP.Williamson and GL.Emmert. ***Anal Chim Acta***, 792:72, (2013).

[12] S.Badilescu and M.Packirisamy Polymers 4, 1278, (2012).

[13] M.C.Yebra-Biurrun, Flow injection analysis of marine samples, published by Nova Science Publishers, Inc. New York, 324,(2009)

[14]M. Bowden, M. Sequeira, J.P. Krog, P. Gravesen and A. Diamond, **Analyst,** 127,4(2002)

[15] M. Bowden, M. Sequeira, J.P. Krog, P. Gravesen and A. Diamond, ***J.Environ.Monti***, 4, 767,(2002)

[16] P.Watts and C. Wiles, ***Journal of chemical research***, 36 (4), 181, (2012).

[17] B. Uthuppu, A. Heiskanen, D. Kofoed, J. Aamand, C. Jørgensen, M. Dufva and M. Havsteen , ***Analyst***, 140, 1616, (2015).

[18] E.H Hansen, Talanta, 64,1076,(2004).

[19]P. Kościelniak, M.Wieczorek, J.Kozak J and M.Herman, Anal ***Chim Acta*** 600: 6,(2004).

[20] M. Shukla and S. Arya, ***Green Chemistry & Technology Letters***, 4 (1), 6,(2018).

[21] D.J. Delporta,, S.S. Potgieter-Vermaakb, R.I. McCrindled and J.H. Potgietere, ***S. Afr. J. Chem***., **64**, 251,(2011).

[22] Raquel B. R. Mesquita, Sı´lvia M. V. Fernandes and Anto´nio O. S. S.Rangel, ***J. Environ. Monit.*** 4, 458,(2002).

[23] K.H. Al-Sowdani, ***Marine Mesopotamica***, 9 (1), 157, 1994.

[24] Trojanowicz M. Flow Injection Analysis: Instrumentation and Application, World Scientific Publishing Co. Pte. Ltd., 497,(2000)

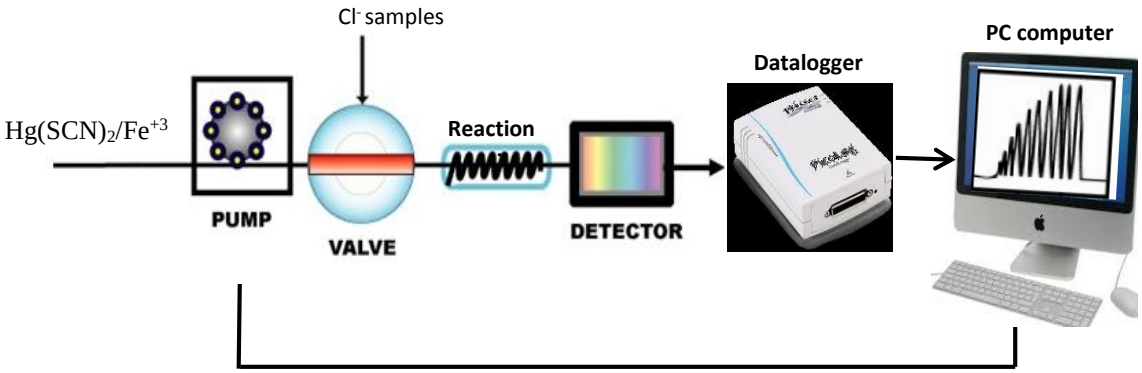
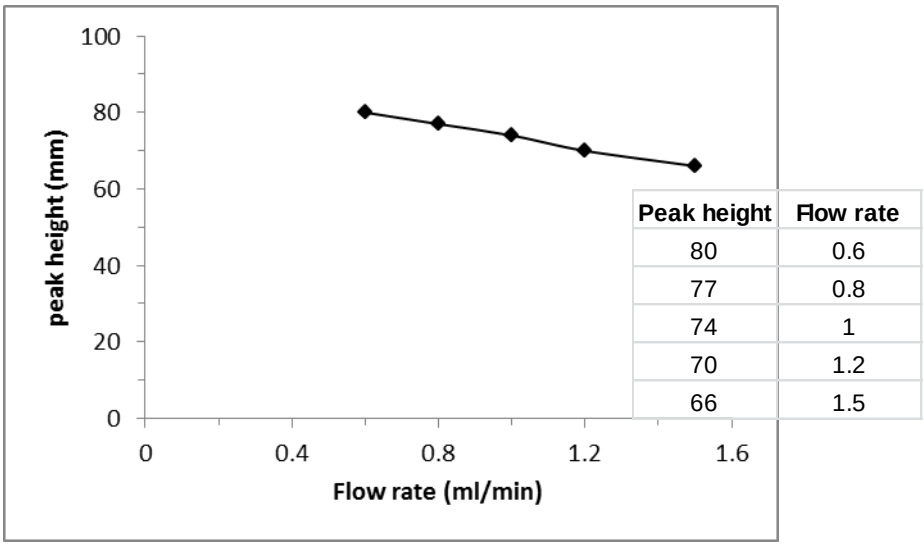
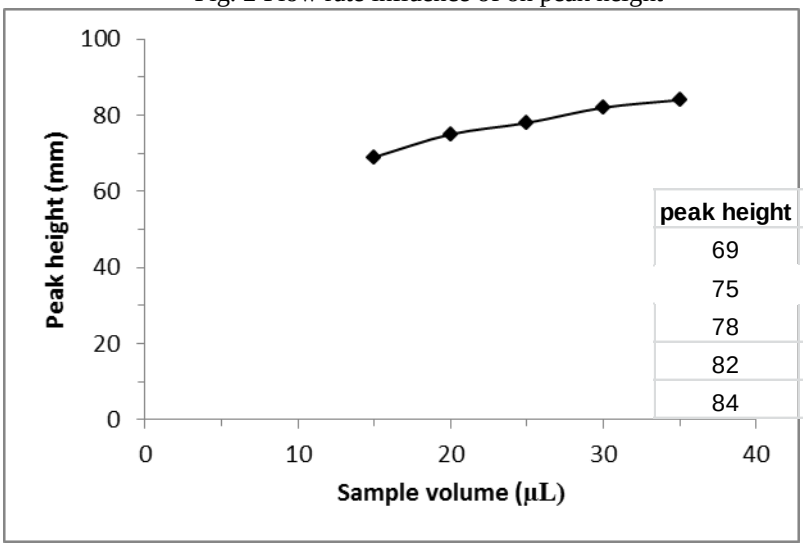


Figure 1 micro- flow injection manifold for chloride determination



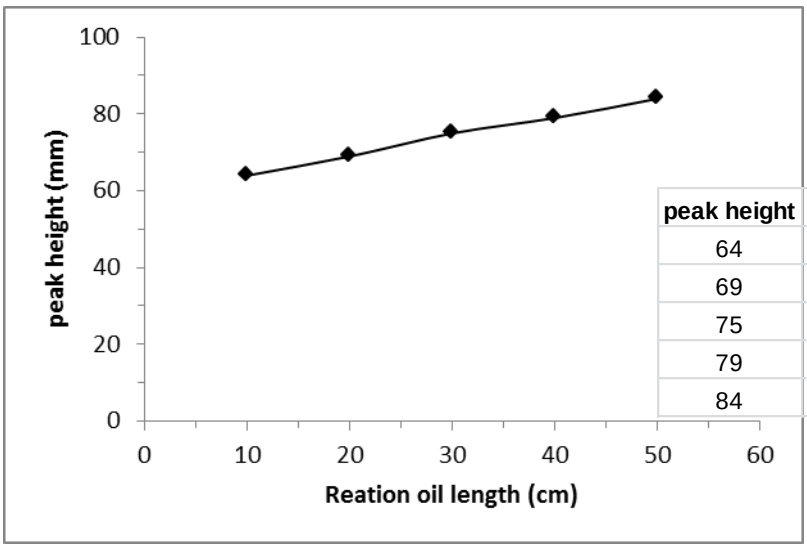
Peak height	Flow rate
80	0.6
77	0.8
74	1
70	1.2
66	1.5

Fig. 2 Flow rate influence of on peak height



peak height	sample volu
69	15
75	20
78	25
82	30
84	35

Fig. 3 Sample volume influence of on peak height



peak height	coil length
64	10
69	20
75	30
79	40
84	50

Fig. 4 Reaction coil length influence of on peak height

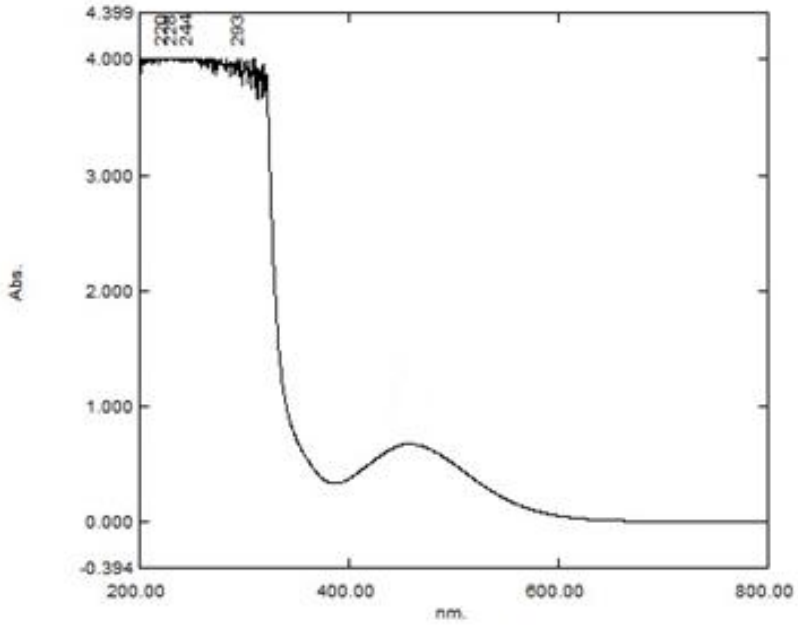


Figure 5 Spectral scans of Iron (III) –Thiocyanate complex

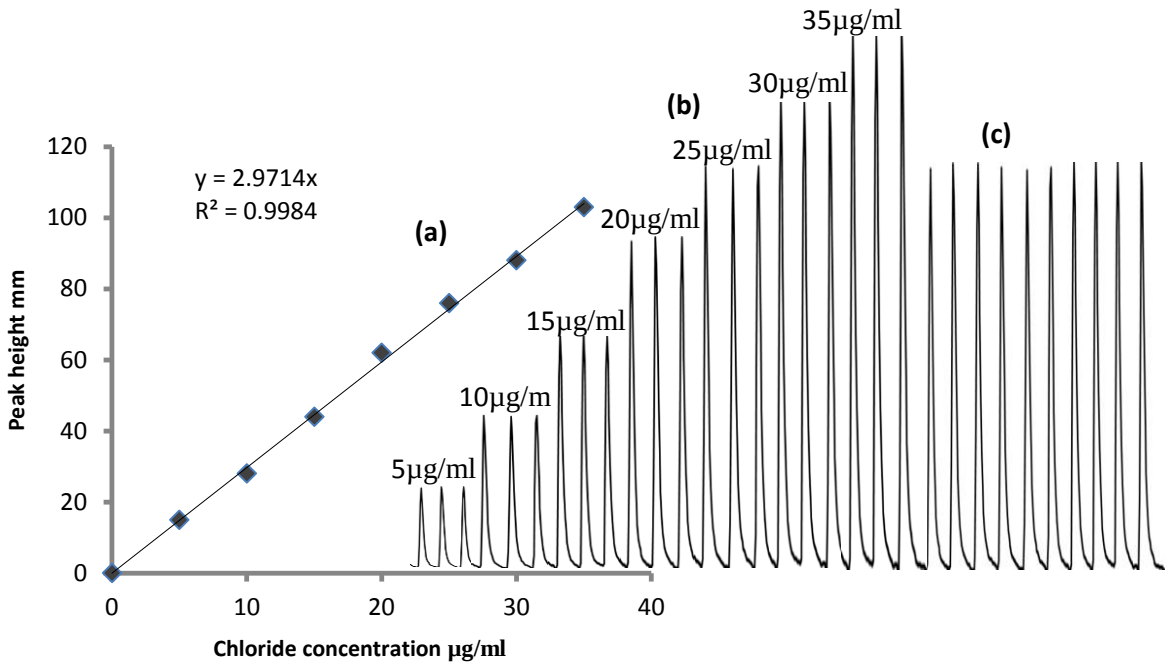


Figure 6: (a). Standard calibration graph for chloride determination. (b). Peaks obtained by injected chloride Standard. (c) 10 replicates of 25 µg\ml standard chloride.

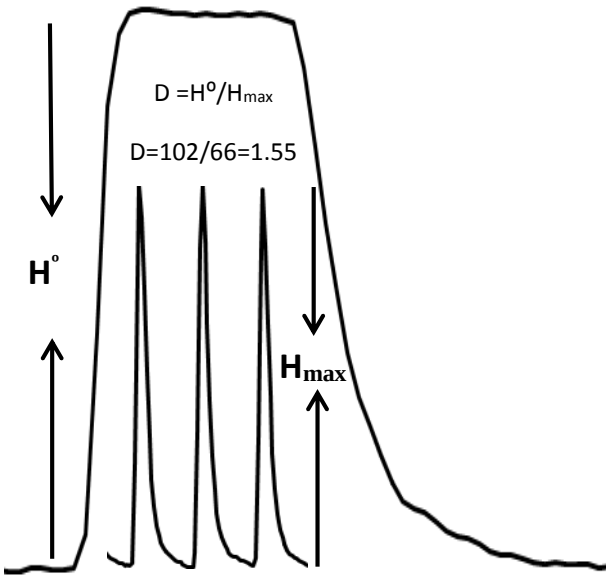


Fig. 7: The dispersion coefficient in flow system

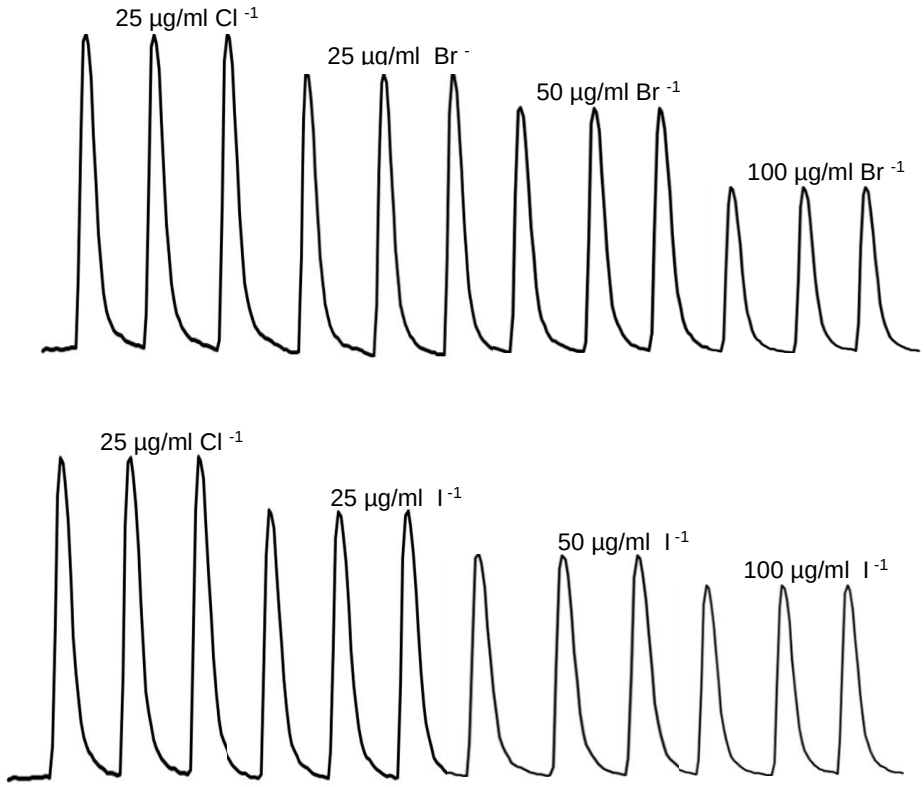


Fig 8: The effect of Bromide and Iodide on peak height for 25 µg/ ml chloride

تطبيق نظام حقن جرياني مايكروي مطيافي محلي الصنع لتقدير الكلورايد في المياه

يوسف شافي جبر الجوراني[1] وكامل حسين السوداني[2]

قسم علوم البحار التطبيقية- كلية علوم البحار- جامعة البصرة –العراق1

قسم الكيمياء-كلية التربية للعلوم الصرفة-جامعة البصرة – العراق 2

Corresponding author: E-mail: yousif.shafi @ yahoo.com

الملخص

تم تصميم وبناء نظام حقن جرياني مايكروي محلي الصنع لتقدير أيون الكلورايد في عينات مياه طبيعية ومياه اسالة جمعت من مياه شط العرب ومدينة البصرة جنوب العراق.تم تصمصم برنامجين للتحكم في عمل نظام الحقن الجرياني المايكروي. البرنامج الأول من نوع UNO للتحكم في عمل المضخة التمعجية المايكروية المحلية الصنع والتي تستخدم لدفع الكواشف الكيميائية الى الكاشف, بينما يستعمل البرنامج الأخر من نوع Mega لتسجيل النتائج على شكل قمم تمثل التركيز باستخدام برنامج مايكروسوفت أكسل 2010 كانت الخطية, معامل الأرتباط لسبع نقاط , حد الكشف ,الأنحراف القياسي لعشر حقنات 30-5مايكروغرام⁄مل ,0.9984, 0.5 مايكروغرام⁄مل,0.0597% على التوالي. كانت سرعة النمذجة 120عينة⁄ساعة. كل عينة تستهلك 94.2 مايكروليتر من الكواشف الكيميائية لذا فأن 120 عينة تستهلك 11.30 مل من الكواشف الكيميائية. تم تطبيق نظام الحقن الجرياني المايكروي الشبه اوتوماتيكي بنجاح مع بساطة في الوحدة المتشعبة وحساسية ودقة عالية في النتائج.

الكلمات المفتاحية: الحقن الجرياني المايكروي. الكلورايد, المطياف الضوئي, شط العرب