ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Designing Flow Injection Unit for Chromates Determining.

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ABSTRACT

This research includes designing flow injection unit for determination chromate . The valve was designed for injection the sample.The optimum condition: volume of sample, flow rate of carrier, dead volume,dispersion coefficient and reproducibility were studied. Best flow rate is 12.30 ml/min,zero dead volume, detection limit = 5 ppm, 2. 84 and high reproducibility for five times respectively . The range of chromate concentration by flow injection analysis was 10 – 70 ppm with R2= 0.999 .

Keywords: Flow injection , Chromate , Dispersion , Dead volume , Dispersion coefficient ,Reproducibility .

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ISSN: 0975-8585

INTRODUCTION

Flow injection is a chemical method of Analysis .It can be distinguished by the simplicity and introduces the help for automatic operating of laboratories [1] . It is also a quick method and it can be used in quantity analysis[2] .it was used at first in medical laboratories and then in different fields of experiments like estimating some of kinds in water, soil, and in air in addition to industry and in different Pharmaceuticals [3] .Many practical theories have been suggested to make it easy to use that method [4] .In 1975 , Hansen &Ruziicka published many researches regarding that method in Denmark and also the scientist Steward did the same in U.S.A. [5] figure (1) It represents a form of the unit .

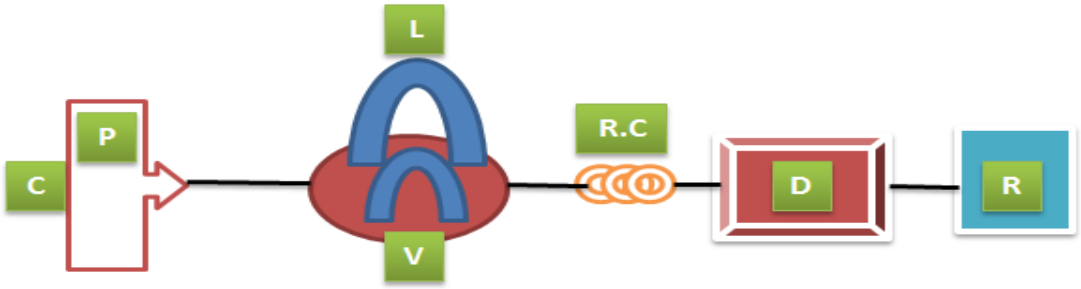

Figure (1) A simple scheme for the flow injection unit

(C = Carrier , P = Pump , L = loop Injection , v= valve , R.C = reaction coil ,D= detector , R= signal recorder)

There are many properties for this method, the parts of the system are easy to be collected because they are cheap limited samples may be used [6] and it depends on using a very little amounts of the sample [7] and the reagent [8] .This technique spends a very little period of time for analysis and it provides an easy method for doing many analytical operations [9] . This process occurs through a closed system that helps getting rid of external conditions, therefore it spreads largely and quickly [10], and gives high Iterative [11] and disposing of classical open systems and its problems [12] .

The principle of FIA is a simple system injecting limited amounts of the sample continuously in a stream then the output is transferred after the occurrence of the reaction to the detector ,where we get the signal through the absorbance change or any other factor after passing through customized flow cell [13].

Chromate a name that is released by Universal Naming System (IUPAC) and its chemical form is $(Cr_2O_4)^{-2}$, and the oxidative number is (- 2) and the molar mass (115.994 g. Mole -1) and its color is yellow . Their aqueous solutions have the status of an alkaline and have many uses in the manufacturing of dyes and leather industry . It is usually used as an analytical reagent or directory . It is one of the carcinogenic compounds like other of all the chromium (III) compounds and they are toxic, so we must handle with it in an extreme caution [14 , 15] . Noting the following equation

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

It is observed there are chemical equilibrium between chromate and dichromate in aqueous solutions (chromate to dichromate turns in the acidic surrounding) . The equilibrium depends on the concentration of chromium where we can observe chromate ion as the predominant type in alkaline solutions and dichromate ion is the prevalent in acidic solutions .The chromate and dichromate are of strong oxidizing agents which generally add three electrons to an atom of chromate to change it into tri chromate [16- 18]

$$Cr_2O_7^{-2} + 14H_3O^+ + 6e^- \longrightarrow 2Cr^{+3} + 21H_2O \qquad \varepsilon_0 = 1.33\ V$$

The possibilities of chromate oxidation in alkaline solutions are weaker than that of acidic ones .

$$CrO_4^{-2} + 4H_2O + 3e^- \longrightarrow Cr(OH)_3 + 5\ OH^- \qquad \varepsilon_0 = -0.13\ V$$

ISSN: 0975-8585

Chromate paints prevent oxidation (rust) on metal surfaces, and it mostly used for coating aluminum, Zinc, copper, cadmium, silver, tin and its alloys . The main source of concern is when you use a chromate as a coat because of its poisonous and the ability to access to the cell easily . Many hazardous waste places contain chromate which possibly pollute the air or the close water sources and it could threat the health and safety of workers . And it is possible to be spread in the wastewater . And the process of removal them is difficult exercise because of the cost and problems of health and safety . The chromate conversion to non-toxic chromate and its use in paint and other offers of government labs and industry eliminating hazardous waste sources with cost savings in the treatment of these wastes and their disposal [19 , 20] .

EXPERIMENTAL

Apparatus , Material and reagents :

1. Chemicals : K_2CrO_4 70 ppm , Carrier is diluted hydrochloric acid (0.1 M) , KI 100ppm , starch (2g in 150 ml water).
2. Equipments : prestatic pump (ISM796 , Switzerland), Home made injection valve , flow injection cell (Helma), spectrophotometer (Aple PD-303UV ,Japan) ,Spectrometer (T80 UV/VIS China), Kompensograph (C1032 , simens ,Netherlands) and Teflon tubes.
3. Method : The carrier is diluted HCl and the sample was injection to valve into the sample loop . The absorbance was measured at (595 nm) . Recorder reads this absorbance as a peaks.
4. The Design of unit to determining chromate

Unit :

The new unit has been made of cheap and available materials and easy to be made as well as environmentally ineffective when destroyed . It is easy to handle any flaw in one of its parts so the system is shown in (Figure 2) which composed of [21- 24] :

1. Peristaltic pump
2. Injection valve
3. Reaction coil
4. Detector
5. Recorder

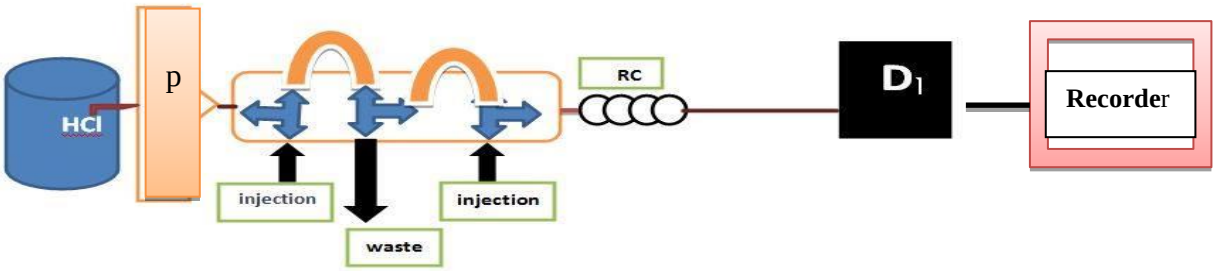

Figure (2) The form of the system used to determine chromate

figure (3) Show steps of injection starch , step (1) enter starch in the first control unit after injection starch by syringe , step (2) move starch inside loop , step (3) enter starch in the second control unit , step (4) way out the excess from starch to outside the unit then close control unit .

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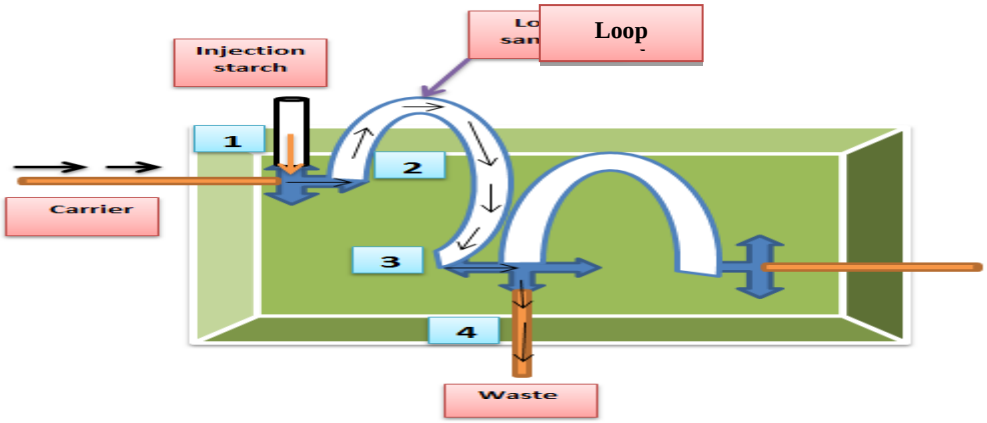

Figure(3) Steps of injection starch by moving 1,2, 3,4 positions

figure (4) Show steps of injection sample , step (1) enter sample in the first control unit after injection sample by syringe , step (2) move sample inside loop , step (3) enter sample in the second control unit , step (4) way out the excess from sample to outside the unit then close control unit .

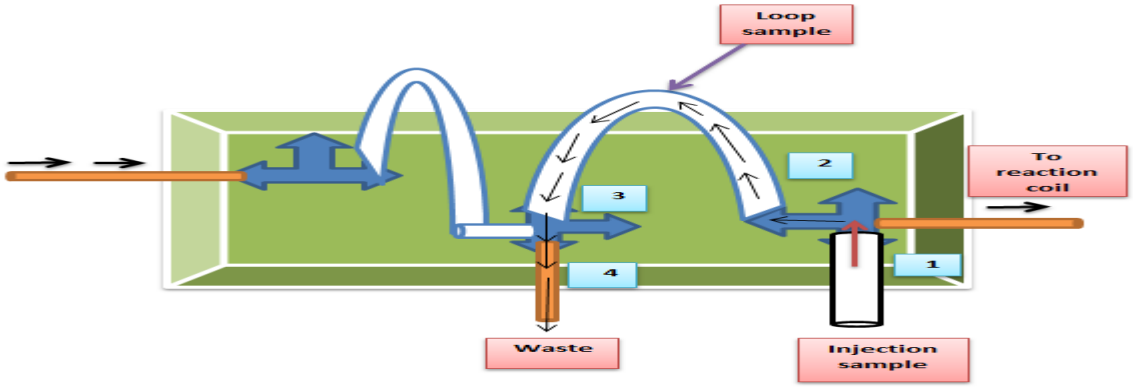

Figure (4) Steps of injection sample by moving 1,2, 3,4 position injection

Figure (5) Show the final unit used in this work .

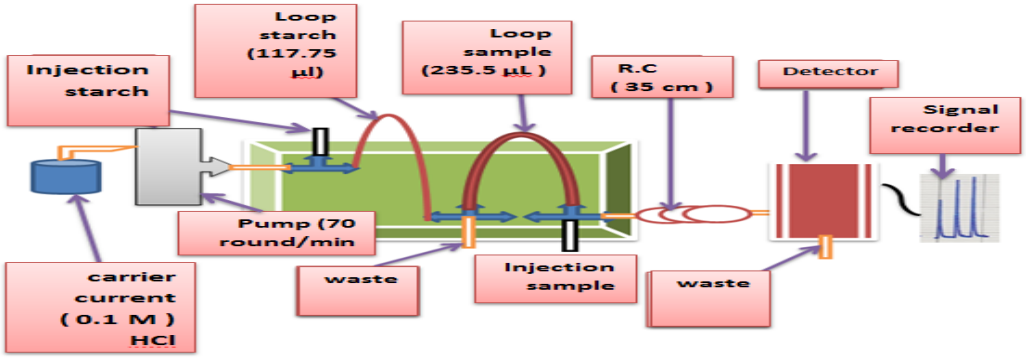

Figure (5) The final outline of the proposed unit used to determine chromate

RESULTS AND DISCUSSION

Effect of flow rate has been studied and the best flow rate was chosen using initial conditions as follows : [(KI) = 100 ppm , (K_2CrO_4) = 70 ppm , (HCl = 5 drops)] , [Starch] = 2 g in 150 ml water , starch loop volume =

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196.25 µl , sample loop volume = 235.5 µl , Length of reaction coil (75 cm) , Flow rate of (20-90 Round / min) , Carrier is diluted hydrochloric acid (0.1 M) .

Table (1) Effect flow rate

Flow rate Round / min	Flow rate /min ml	Response cm	Response cm	Response cm	the average cm	S.D	R.S.D%
20	3.300	1.200	1.100	1.100	1.000	0.100	0.090
30	4.900	1.300	1.500	1.500	1.433	0.115	0.076
40	6.600	1.800	2.000	2.000	1.933	0.115	0.056
50	8.100	2.600	2.600	2.600	2.600	0.000	0.000
60	10.000	2.800	2.900	2.900	2.866	0.057	0.019
70	12.300	3.300	3.300	3.300	0.300	0.000	0.000
80	13.700	1.300	1.200	1.300	1.230	0.180	0.146
90	14.800	1.400	1.100	1.000	1.160	0.120	0.103

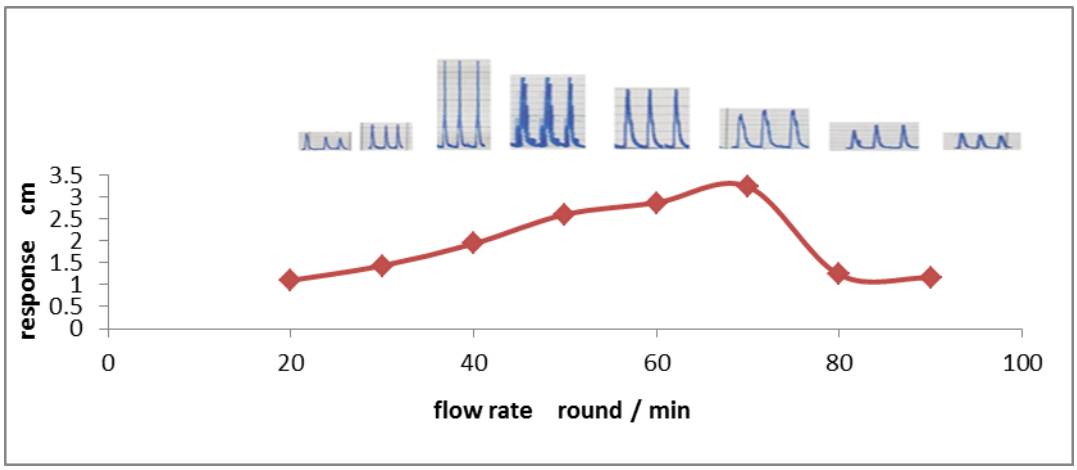

Figure (6) Effect flow rate

Through clear responses in Figure (6) ,it is noted an increase in the peak high with the increase in flow rate because of the reduced physical variables and the most important one is the dispersion until access to speed (70 cycles / minute) and it is followed by a decrease in response that shows us that the high velocity will not be suitable because they do not give us enough time to study this reaction .

Effect of reaction coil : All that made of glass with different lengths . where that reaction coil have a significant impact on the sensitivity of the way at a fixed initial conditions: [(KI) = 100 ppm , (K_2CrO_4) = 70 ppm , (HCl = 5 drops)] , [Starch] = 2 g in 150 ml water , starch loop volume = 196.25 µl , sample loop volume = 235.5 µl

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, Length of reaction coil (35 – 120 cm) , Flow rate of (70 Round / min) , Carrier is diluted hydrochloric acid (0.1 M) .

Table (2) Effect of reaction coil

Reaction coil (cm)	Response cm	Response cm	Response cm	the average cm	S .D	R.S.D %
With out	1.200	1.200	1.200	1.200	0.000	0.000
35	2.600	2.600	2.600	2.600	0.000	0.000
55	3.700	3.700	3.700	3.700	0.000	0.000
75	3.100	3.300	3.300	3.233	0.115	0.035
100	2.400	2.400	2.300	2.366	0.075	0.024
120	1.300	1.300	1.300	1.300	0.000	0.000

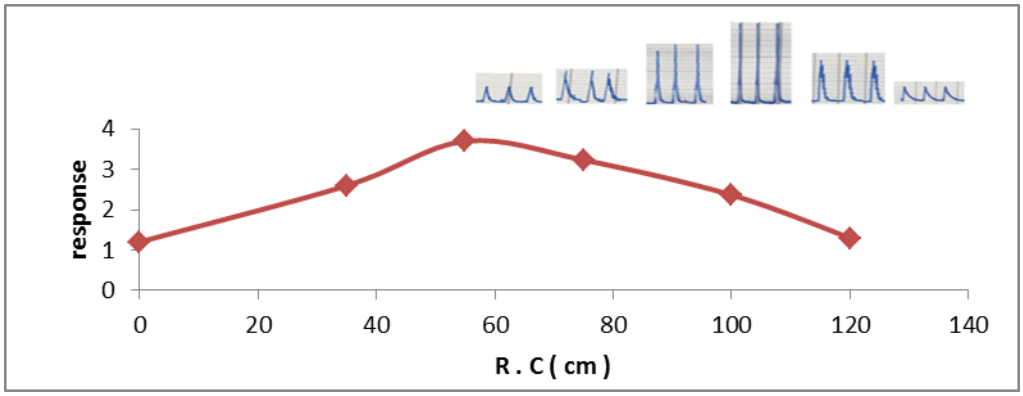

Figure (7) Effect of reaction coil length

The experiment started from the non-use of reaction coil in the system and it is found that there is a response. But there is a problem in the process of washing and increasing the length of the coil to improve the signal (more clarity peak).It is observed that the best response when the length of the coil is (55 cm) and when we use the more reaction coil lengths than (55 cm) there response but not considered the best which shows that the fast interaction and does not require mixing of many .

Effect of sample volume (loop sample) :

The (V) can be calculated through the cylinder volume rule ($V = \pi r^2 L$) (V= volume , π = 3.14 , r = radius loop , L = Length loop) and other conditions are constant according the following : [(KI) = 100 ppm , (K_2CrO_4) = 70 ppm , (HCl = 5 drops)] , [Starch] = 2 g in 150 ml water , starch loop volume = 196.25 µl , sample loop volume = (20 – 35 cm) , Length of reaction coil (55 cm) , Flow rate of (70 Round / min) , Carrier is diluted hydrochloric acid (0.1 M)

Table (3) Effect of sample volume

Sample volume Ml	sample Loop	response cm	response cm	response cm	the average cm	S.D	R.S.D %
157.000	20	1.900	1.900	1.800	1.866	0.075	0.030
196.250	25	2.200	2.200	2.100	2.166	0.075	0.026
235.500	30	3.700	3.700	3.700	3.700	0.000	0.000
274.750	35	1.700	1.700	1.700	1.700	0.000	0.000

ISSN: 0975-8585

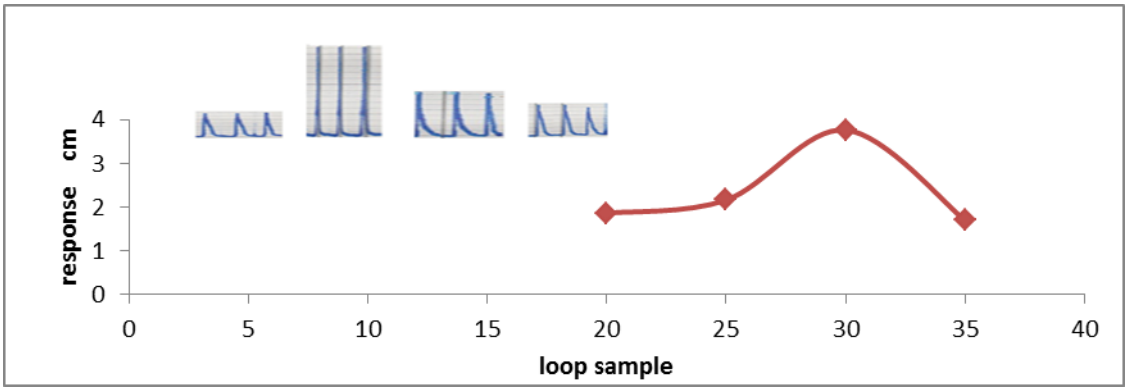

Figure (8) Effect of sample volume

It is observed that there is an increase in the response of the length of the loop (20-30) then we get a decrease in it . We conclude that the best length for the mixture load loop is (30) because it gave the best response and a high corresponding .

The effect of starch volume (loop starch):

The use of different lengths of loop to starch after installing along the loop mix download (hydrochloric acid and potassium iodide and potassium chromate) at (30) are calculated as stated volume of the Code of the volume of the cylinder. Other conditions have been installed, according to the following: [(KI) = 100 ppm , (K_2CrO_4) = 70 ppm , (HCl = 5 drops)] , [Starch] = 2 g in 150 ml water , volume loop starch = (15 – 20 – 25 – 30 cm) , volume loop sample = (30 cm) , Length of reaction coil (55 cm) , Flow rate of (70 Round / min) , Carrier is diluted hydrochloric acid (0.1 M)

Table (4) Effect of starch volume

Volume of sample	Loop starch	response cm	response cm	response cm	The average cm	S.D	R.S.D %
117.750	**15**	**5.600**	**5.600**	**5.600**	**5.600**	**0.000**	0.000
157.000	**20**	**4.500**	**4.300**	**4.300**	**4.366**	**0.013**	0.114
196.250	**25**	**3.700**	**3.700**	**3.700**	**3.700**	**0.000**	0.000
235.500	**30**	**2.800**	**2.700**	**2.700**	**2.733**	**0.057**	0.020

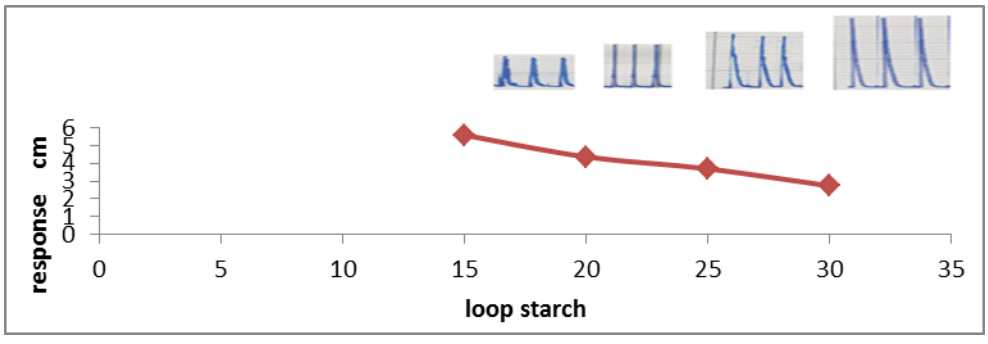

Figure (9) Effect of starch volume

We observe that the best response will be when the length of loop is (15) as well as loop (20), but loop (15) gave us a clear peak without distortions, and loop (20) despite the obvious response, we observe the distortions of the peak when the washing process, indicating the difficulty of removing the starch in the washing process .

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Calibration:

After installing all the conditions, the calibration curve has been studied to determine the chromate where several solutions of concentrations of chromate (10 -90 ppm) were prepared and the conditions that have been installed to study the calibration curve are: [(KI) = 100 ppm, (K_2CrO_4) = 10-90 ppm ,(HCl = 5 drops)],[Starch] = 2 g in 150 ml water ,volume starch (115.75µl) ,volume sample = (235.5 µl), Length of reaction coil (55 cm) , Flow rate of (70 Round / min) ,Carrier is diluted hydrochloric acid (0.1 M) .

Table (5) Calibration curve

Con. chromate Ppm	response cm	response cm	response cm	The average cm	S.D	R.S.D %
10	**0.900**	**0.900**	**0.900**	**0.900**	**0.000**	0.000
20	**1.800**	**1.700**	**1.700**	**1.733**	**0.057**	0.028
30	**2.500**	**2.400**	**2.400**	**2.433**	**0.057**	0.021
40	**3.300**	**3.200**	**3.200**	**3.233**	**0.057**	0.017
50	**4.200**	**4.100**	**4.100**	**4.133**	**0.057**	0.013
60	**4.800**	**4.800**	**4.800**	**4.800**	**0.000**	0.000
70	**5.600**	**5.600**	**5.600**	**5.600**	**0.000**	0.000
80	**6.500**	**6.400**	**6.400**	**6.433**	**0.057**	0.009
90	**7.400**	**7.400**	**7.400**	**7.400**	**0.000**	0.000

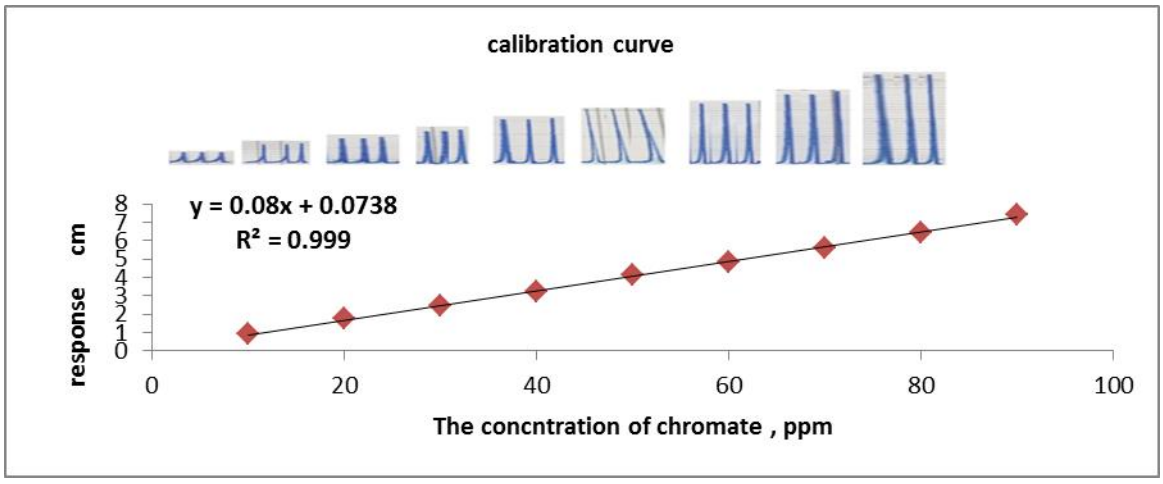

Figure (10) Calibration curve

Reproducibility:

When you install conditions. [(KI) = 100 ppm , (K_2CrO_4) = 70 ppm , (HCl = 5 drops)] , [Starch] = 2 g in 150 ml water , volume loop starch = (15 cm) , volume loop sample = (30 cm) , Length of reaction coil (55 cm) , Flow rate of (70 Round / min) , Carrier is diluted hydrochloric acid (0.1 M) . We studied reproducibility

Table (6) Studied reproducibility

Response	The average	S.D	R.S.D %
2.800	2.840	0.077	**0.027**
2.800			
2.800			
2.900			
2.900			

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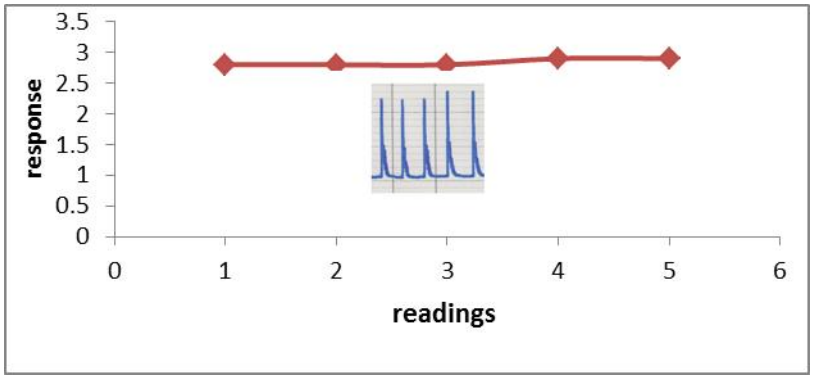


Figure (11) Studied reproducibility

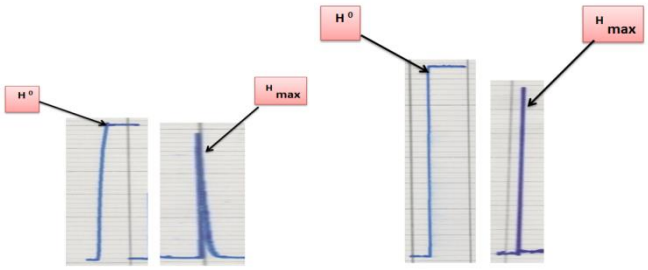
Dispersion coefficient :

The dispersion coefficient was studied at 595 nm , [(KI) = 100 ppm , (K_2CrO_4) = 70 ppm , (HCl = 5 drops)] , [Starch] = 2 g in 150 ml water , volume loop starch = (15) , volume loop sample = (30) , Length of reaction coil (55 cm) , Flow rate of (70) , Carrier is diluted hydrochloric acid (0.1 M) . The absorbance was measured with dispersion H_{max} and without dispersion H^O as showed in table (7) .The absorbance experimentally decrease with dispersion . The dispersion coefficient (D) was calculated from following equation as showed in figure 12 [25 – 27] .

$$D = H^O / H_{max}$$

Table (7) Effect of dispersion

Con. of chromate	H^0	H_{max}	D
30 ppm	**7.300**	**7.000**	1.042
60 ppm	**9.000**	**8.700**	1.045



) b) (a (

Figure (12) Effect of dispersion (a) at 30 ppm , (b) 60 ppm

Dead volume:

The place made valve which used in this work has a zero dead volume . Where all responses start from zero baseline for one response. This case is perfect in our work and this accomplished to the past work in FIA lab .

(a) (b) (c)

Figure (13) Dead volume

ISSN: 0975-8585

(a) at injection K_2CrO_4 + Starch + HCl
(b) at injection K_2CrO_4 + Starch + KI
(c) at injection KI + Starch + HCl

CONCLUSIONS

FIA unit which used in this work was Cheap and gave a good results for determining chromate by using a small volume of th sample and very good output sampling comparing with spectrophotometric method.

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