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Research Article

NEW DESIGN OF FLOW INJECTION UNIT FOR DETERM/NATION ALUMINUM (III) BY ALIZARIN DYE

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Abstract

A new simple and rapid method is reported for the accurate and precision spectrophotometric determination of Aluminum (III) using flow injection analysis (FIA). The study includes using Alizarin for determination Aluminum(III) the various parameters; physical and chemical affecting on determination have been investigated such as flow rate, reaction coil, volume of reagent (Alizarin), volume of sample, pH and concentration, then preparation the calibration curve, the dispersion coefficient, reproducibility, Interferences and application were studied. the method is based on determination Aluminum(III) by Alizarin which was determined spectrophotommetrically at 494nm, the method allows the determination of linear range (2-140) mg/l and the sampling rate of 120 sample per hour, the detection limit (0.5 mg/l) for FIA. Relative standard deviation for (60mg/l), n=10 for the method is found (0.274% for FIA). Dispersion coefficient is measure for the method.

Keywords: determination, Flow injection, Alizarin dye, Aluminum (III).

Introduction

One of the important versatile instrumental tool that contributed substantially to the development of automation in pharmaceutical analysis due to its simplicity, low cost and relatively short analysis time is The flow injection analysis (FIA)[1].Ruzicka and Hansen conceived The pioneering and still largely used flow injection analysis (FIA), in 1975[2].Conventional FIA analyzers have been designed as closed and dedicated systems useful to work with very well defined sample compositions [3] .In 1990(FIA) developed based on forward, reversed, and stopped flow of the carrier stream and it has been the subject of several studies aimed to establish its theory and particularities by Ruzicka and Marshall [4].The same principles as FIA (controlled partial dispersion and reproducible sample handling)This technique for automatic sample analysis is based on too [5]characterizations of Flow injection technique are simplicity , speed, and lack of cost as it is based on the use of trace amounts of reagent [6] and symmetry high in the analysis process in a way automatic or semi-automatic and highly efficient and fast distinct and sensitive to chemical analyzes and the number of modeling large and limits of detection of low-lying [7].Alizarin (1,2-dihydroxy-9,10-anthraquinone) Anthraquinone derivatives is one of the promising indicators for low-polar solvents is in general are known as analytical reagents, Alizarin itself is applied in chemical analysis as well. The absorption maximum of the neutral non-dissociated form is located at 430 nm [8-14].Is a non- essential trace element of ubiquitous distribution. It is the third most abundant metal ion in the biosphere comprising about 8% of the earth's crust[15]For the determination of aluminum bybromooxine, pyridylazoresorcinol (PAR), 1-(2-pyridylazo)-2-naphtol (PAN) have been used for spectrophotometric determination of indium. But, these reagents are less sensitive (ε = 8.8×10^3, 4.3×10^4, 1.9×10^4 L mol^{-1} cm^{-1},respectively)[16]. the new method has been developed for the determination of aluminum with 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo) quinoxaline (DCHNAQ) which have synthesized by us and the method has been applied to the determination of

aluminum in certified steel, alloys, waste water, river waters, spring water and ground water samples[17].Aim this study the determination aluminum (III) by alizarin dye in new design of flow injection unit.

Materials and Methods

Analytical Balance sensitive Denver Instrument, Spectrophotometer Labomed In G single beam, USA, and a spectrophotometer ShimadzuUV-1700 spectrophotometer, Recorder Pen Siemens C 1032, Hitter thermal Ardeas 51, peristaltic pump Germany, Ismatic, Teflon tubes with the radius of 0.5 mm, homemade valves, flow cell volume of 450 µL, pH meter, WTW 720.

Chemicals

1- Prepared2000 mg/l of Aluminum ion (as stock solution) by dissolved (24.7103)g of $[Al_2(SO_4)_3.18H_2O]$in (1000) ml of distilled water with adding (1)ml of H_2SO_4 Concentrated(18), and then prepared other solution at used dilution law.

2- Preparation of 0.001 M of Alizarin Dye by dissolved (0.0240) from Alizarin Dye in the beaker by 50 mL of distilled Alcohol then transferred to volumetric flask capacity 100 ml and complete to mark with distilled water.

3- Preparation buffer solution pH=7 [0.1M Sodium Carbonate + 0.2M hydrochloric acid] was weight (2.5g)from Sodium Carbonate at distilled water in the beaker 50 mL was transferred to volumetric flask capacity 250 ml and complete to the extent of the mark with distilled water and Prepare 0.2 M of hydrochloric acid by used dilute low from concentration reagent has S.G (1.8) and purity (36-37.5)% after prepare solution standrazation with carbonate solution[18].

Results and Discussion

Determine the max wavelength

Been determined wavelength greater complex using ultraviolet visible spectroscopy to found λ_{max} for reagent and complex and then determined the optimum conditions for the complexity. In this study found λmax of dye 432 nm and complex [Al(III) with Alizarin] is 494 nm as fig .1.

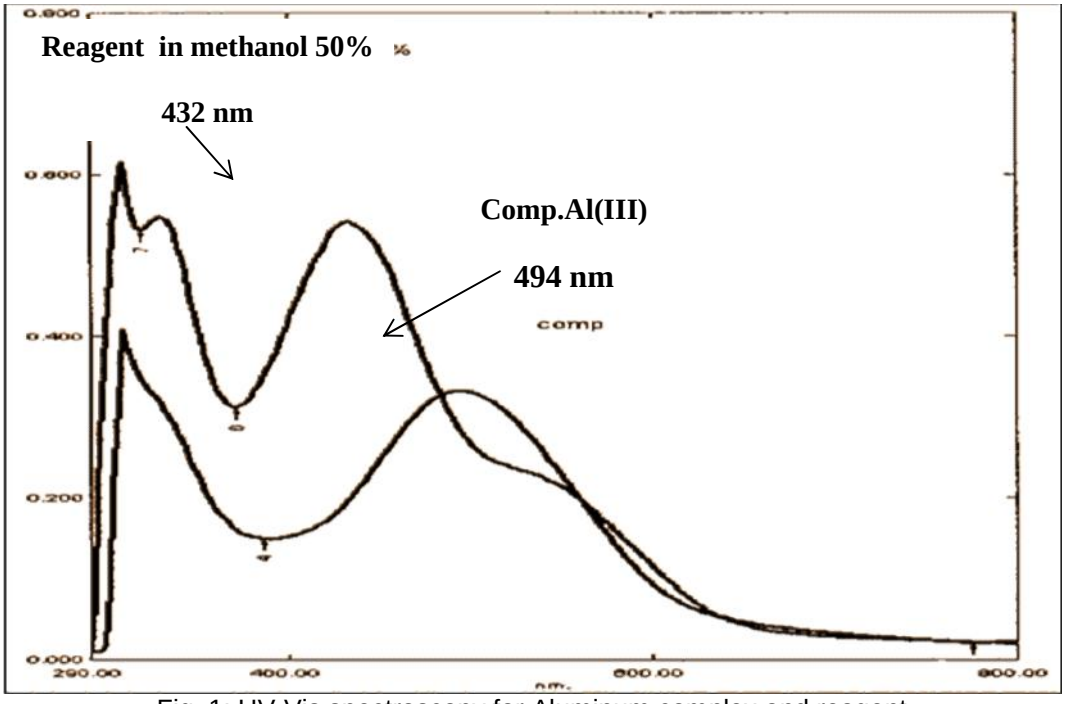

Fig. 1: UV-Vis spectroscopy for Aluminum complex and reagent

The design Flow injection unit

To found the typical design for determining of ion as shown fig .2,

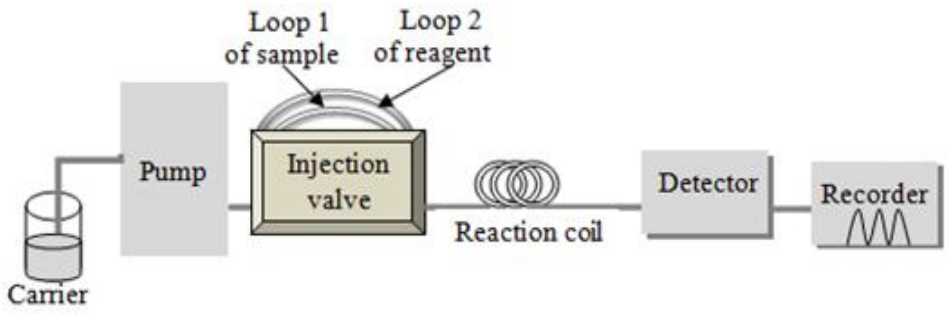

Fig .2 :New design of FIA at :flow rate=9.0ml min^{-1},reaction coil=50cm,Al (III) concentration =20ppm, Alizarin concentration =0.001M.

in this unit used each the following solutions:
1-Reagent dissolvent in ethanol, found the peak height=8.68mm
2- Reagent dissolvent in methanol , found the peak height=5.04mm
3-Reagent dissolvent in methanol+ water (1:1), found the peak height=2.11mm
The study showed that the best signal in the following measurements is when the solvent is methanol and water in a ratio of 1:1.this gives peak shape and less than other solvent in peak height.

Unit

The various parameters affecting the unit have been investigated and selected for a final method evaluation; the following results allow the operator to choose different operation conditions.

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Physical Parameters

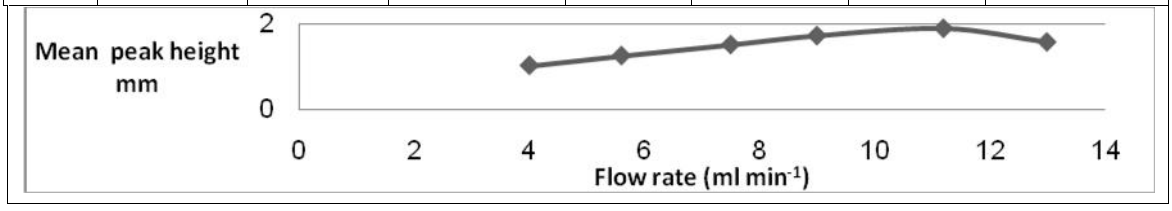
Effect of the flow rate

The effect of the flow rate on the peak height was studied in the range of (4 - 13) ml min^{-1}.as in table 1 and fig. 3.Lower flow rate cause doublet peaks, possibly due to the fact that the carrier solution did not sufficiently disperse into the middle of the sample zone [19]. On other hand the peak height decreased with the increasing of the flow rate [21,20]. Taking into consideration of the stability of the pump, peak shape and sampling time, the flow rate of the carrier solution was adjusted to 11.2 ml min^{-1}. For subsequent measurement due to highest sensitivity

Table 1: Effect of the flow rate on the peak height at:
Al (III) con. =20ppm, R.C (reaction coil) = 30 cm, [Alizarin] =0.001M, and sample loop (L_1) = reagent loop (L_2) =30cm

Fig.3: Change the peak height with flow rate

No	flow rate ml min^{-1}	Peak	Height	Mm	Mean	S.D	RSD%
1	4.00	1.02	1.02	1.02	1.02	0.00	0.00
2	5.600	1.25	1.25	1.25	1.25	0.00	0.00
3	7.500	1.52	1.50	1.52	1.51	0.01	0.66
4	9.00	1.72	1.72	1.72	1.72	0.000	0.000
5	11.20	1.86	1.87	1.89	1.87	0.01	0.53
6	13.00	1.56	1.56	1.60	1.57	0.02	1.36



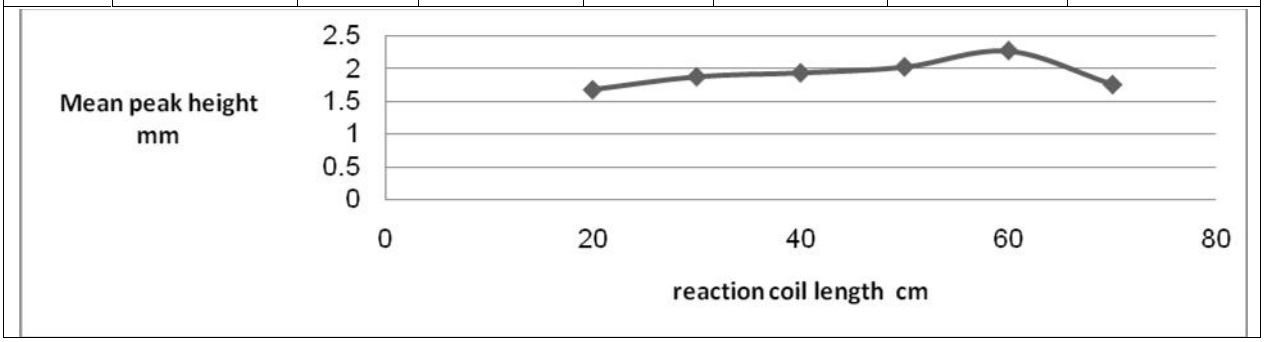
Effect of the reaction coil length

The absorbance as the peak height as table 2 and fig. 4shows effect the reaction coil length on the peak height in the range (20-70) cm it was seen the suitable reaction coil length 60 cm ,since it provided the greatest sensitivity.

Table 2: Effect of the reaction coil length on the peak height at: Al (III) con. =20ppm, flow rate (11.20 ml min. $^{-1}$), [Alizarin] =0.001M, and sample loop (L_1) =reagent loop(L_2) =30cm

Fig.4: Change the peak height with the Reaction coil

No	reaction coil length	Peak	height	Mm	Mean	S.D	RSD%
1	20	1.66	1.70	1.66	1.67	0.02	1.20
2	30	1.87	1.87	1.87	1.87	0.00	0.00
3	40	1.92	1.94	1.93	1.93	0.01	0.52
4	50	2.01	2.03	2.02	2.02	0.01	0.49
5	60	2.27	2.26	2.27	2.27	0.01	0.44
6	70	1.75	1.75	1.75	1.75	0.00	0.00



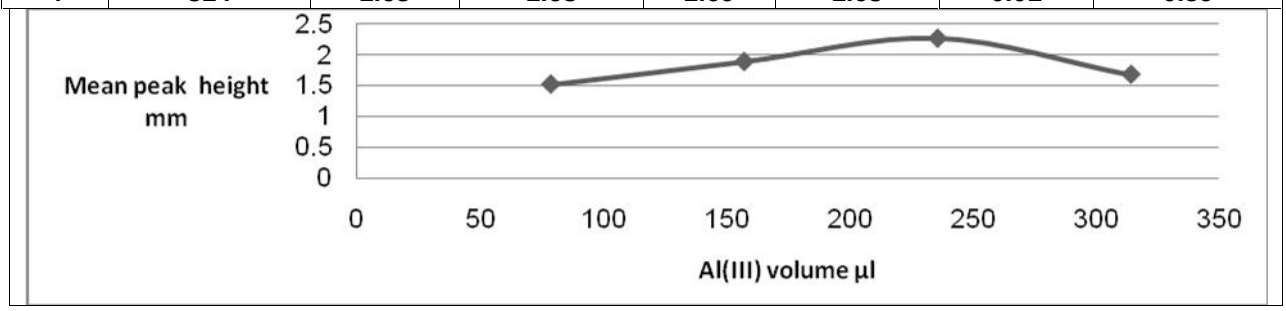
Effect of the sample volume

The influence of the sample volume on the peak height was investigated by injecting different volumes (78.5 -314) µL. The peak height increased to the maximum at 235.5 µL after that volume the peak height decreased, so that 235.5µL was chosen f**o**r further work as table 3 and fig.5.

Table 3: Effect of the sample volume on the peak height at: Al(III)con. =20ppm, flow rate (11.20 ml min. $^{-1}$), [Alizarin] =0.001M, Alizarin loop (L_2) = 30 cm and reaction coil length= 60 cm

Fig .5: Change the peak height with sample volume

No	Sample volume µL	Peak	Height	Mm	Mean	S.D	RSD%
1	78.50	1.52	1.51	1.53	1.52	0.01	0.66
2	157	1.89	1.89	1.89	1.89	0.00	0.00
3	235.5	2.27	2.27	2.27	2.27	0.00	0.00
4	314	1.68	1.68	1.69	1.68	0.01	0.59



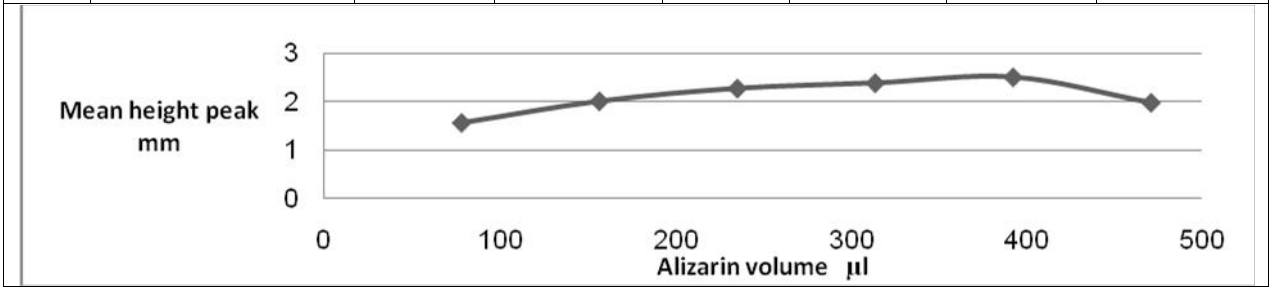
Effect of Alizarin dye volume

The influence of the various volume of Alizarin (78.5 – 471) µL. The Alizarin dye volume that exhibited the greatest peak height was found to be 392.5 µL and was chosen as the optimum as in fig.(6) and table(4).

Table 4: Effect of the Alizarin dye volume on the peak height at: Al(III) con. =20ppm, flow rate (11.20 ml min. $^{-1}$), [Alizarin] =0.001M, sample loop (L_1) = 30 cm and reaction coil length = 60cm

Fig.6: Change the peak height with the Alizarin dye volume

No	Volume Alizarin µL	Peak	Height	mm	Mean	S.D	RSD%
1	78.50	1.57	1.57	1.57	1.57	0.00	0.00
2	157	2.01	2.01	2.01	2.01	0.00	0.00
3	235.50	2.29	2.24	2.29	2.27	0.03	1.23
4	314	2.40	2.38	2.37	2.38	0.01	0.42
5	392.50	2.50	2.50	2.50	2.50	0.00	0.00
6	471	1.99	1.99	1.96	1.98	0.02	1.01



Chemical parameters

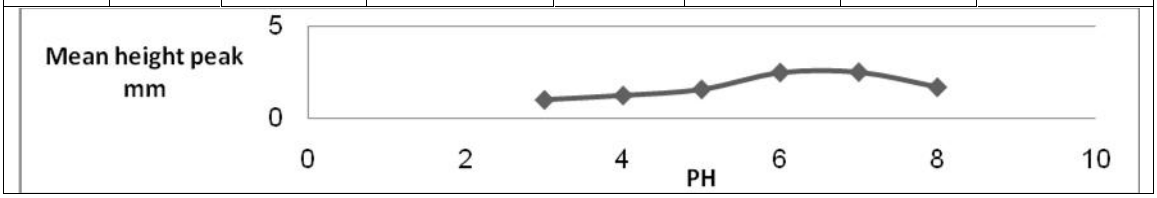
Effect the pH

Determine the pH through the formation of the complex in the different of pH from (3-8), the optimum pH was[6-7], after it prepared the suitable buffer from hydrochloric acid (HCl) and Sodium Carbonate (Na_2CO_3), to adjust the pH of medium, as in the fig.7 and table 5.

Table 5: Effect of the pH on the peak height at: Al (III) con. =20ppm, flow rate (11.20 ml min. $^{-1}$), [Alizarin] =0.001M, sample loop (L_1) = 30 cm, reagent loop (L_2) =50cm and reaction coil length = 60 cm.

Fig.7: Change the peak height with pH

No	PH	Peak	height	mm	Mean	S.D	RSD%
1	3	0.99	0.99	1.02	1	0.02	2
2	4	1.24	1.24	1.24	1.24	0.00	0.00
3	5	1.57	1.56	158	1.57	0.01	0.64
4	6	2.49	2.49	2.49	2.49	0.00	0.00
5	7	2.51	2.51	2.51	2.51	0.00	0.00
6	8	1.68	1.70	1.70	1.69	0.01	0.59



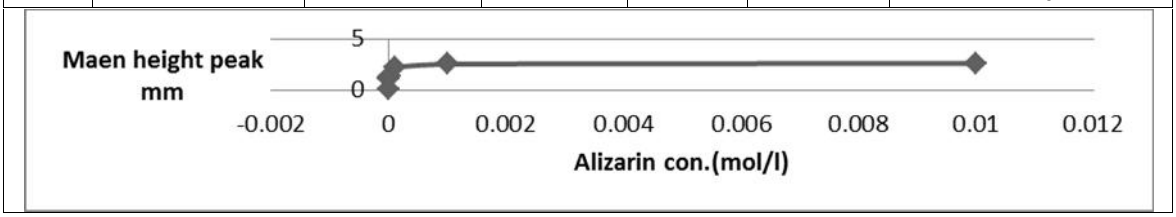
Effect of the reagent concentration

The reagent concentration was varied in the range (1×10^{-8}–1×10^{-2}) M in order to maximize the peak height. table 6 and fig. 8show the effect of reagent concentration on the peak height of the Aluminum(III). The maximum peak height was obtained with $1*10^{-3}$ M reagent, therefore the1×10^{-3}M reagent was chosen for further work at 10^{-2} M occur double peak to this chosen 1×10^{-3}M as best concentrate.

Table 6 : Effect of the reagent concentration on the peak height at: Al (III) con. =20ppm, R.C (reaction coil) = 60 cm, sample loop (L_1) = 30cm, reagent loop (L_2) =50 cm, pH=7, and flow rate=11.20ml min $^{-1}$

Fig.8: Change the peak height with reagent concentration

No	[reagent]	Peak	height	mm	Mean	S.D	RSD%
1	1×10^{-8}	0. 85	0. 85	0. 86	0. 85	0.01	1.17
2	1×10^{-7}	1.13	1.13	1.14	1.13	0.01	0.88
3	1×10^{-6}	1.17	1.18	1.16	1.17	0.01	0.85
4	1×10^{-5}	1.30	1.30	1.30	1.30	0.00	0.00
5	1×10^{-4}	2.17	2.20	2.20	2.19	0.02	0.91
6	1×10^{-3}	2.51	2.51	2.51	2.51	0.00	0.00
7	1×10^{-2}	2.60	2.60	2.60	2.60	Double peak	



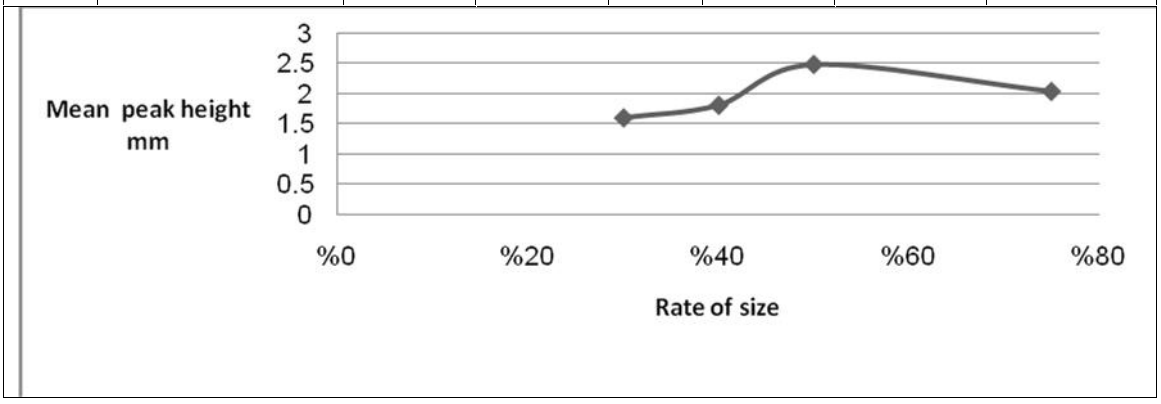
The effect of the composition of the solvent

Has been studied volume ratio of solvent through the use of different ratio of solvent within the range of (75% -30%) of methanol -water to dissolve the dye Fig.9 and table 7 the result shown that, the use of the percentage (50%) of the solvent is the best because it showed best up response Summit.

Table 7 : Effect of the Ratio of solvent on the peak height at: Al (III) con. =20ppm, flow rate (11.20 ml min. $^{-1}$), [Alizarin] =0.001M, sample loop (L_1) = 30 cm, reagent loop (L_2) =50cm and reaction coil length = 60 cm

Fig.9: Change the peak height with Ratio of solvent

No	Ratio of solvent	Peak	height	mm	Mean	S.D	RSD%
1	30%	1.61	1.61	1.61	1.61	0.00	0.00
2	40%	1.83	1.83	1.80	1.82	0.02	1.09
3	50%	2.50	2.50	2.50	2.50	0.00	0.00
4	75%	2.05	2.05	2.05	2.05	0.00	0.00



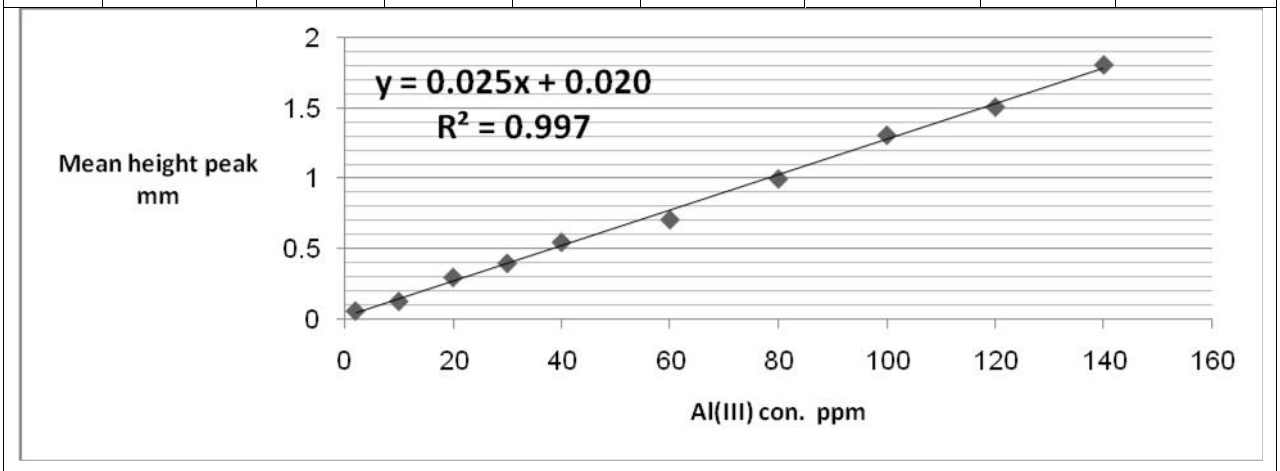
Calibration curve in FIA method

Calibration curve was prepared at the optimum conditions of complexation and change through the metal ion concentration, the result show in table 8 and fig. 10.The calibration curve is linear in the range of 2 - 140 mg l^{-1}. The slope = 0.025 and Correlation coefficient R^2 = 0.997.

Table 8: Effect of the concentration of Al (III) con. with peak height flow rate =11.20ml/min, pH=6-7,reaction coil length=60cm , sample Loop(L_1) =30cm, [Alizarin]=0.001M, and reagent Loop (L_2)=30cm,peak height of Alizarin dye only=2.21mm

Fig.10: Calibration curve of Al (III) with Alizarin in FIA method

No.	Al(III) con. Ppm	Peak height mm			Mean peak height complex Al(III) with Alizarin	The peak height of complex after removal peak of Alizarin	SD	RSD%
1	2	2.27	2.27	2.27	2.27	0.06	0.00	0.00
2	10	2.33	2.33	2.35	2.34	0.13	0.01	0.43
3	20	2.51	2.51	2.51	2.51	0.3	0.00	0.00
4	30	2.61	2.61	2.61	2.61	0.4	0.00	0.00
5	40	2.67	2.76	2.76	2.76	0.55	0.000	0.00
6	60	2.94	2.94	2.88	2.92	0.71	0.03	1.03
7	80	3.21	3.21	3.20	3.21	1.00	0.01	0.31
8	100	3.53	3.52	3.51	3.52	1.31	0.01	0.28
9	120	3.72	3.72	3.71	3.72	1.51	0.01	0.27
10	140	4.02	4.02	4.02	4.02	1.81	0.00	0.00

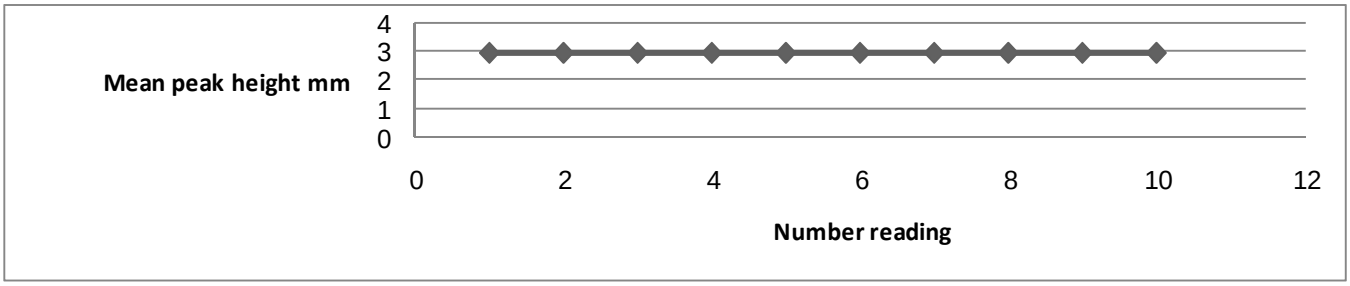


Reproducibility

For study prevision range and method effective using in determination of Aluminum (III) from through reproducibility injection and measure for multitimes, use 60 ppm, so that arrived amount standard deviation for (60 mg/L), n=10 (0.008) and amount relative standard deviation (0.274%) so that accuracy and effective system for determination the ion, the result show in table 9 and fig. 11.

Table 9 : Reproducibility for 30ppm of Al (III)
Fig. 11: Reproducibility Al (III) for 30 ppm with Alizarin

No.	1	2	3	4	5	6	7	8	9	10	Mean	S.D	RSD%
Peak height	2.92	2.93	2.91	2.93	2.91	2.93	2.92	2.92	2.91	2.92	2.92	0.008	0.274



From the result of Reproducibility study ,the detection limit calculate depend on the law (D.L= (3×con. ×S.D.)/ mean) and was 0.5mg / l .

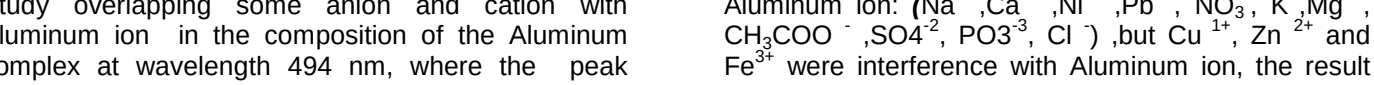
Determination of Dispersion

To measure the dispersion value in different sample zones of (60 and 100 ppm) Aluminum ion for FIA, two experiments were carried out. In the first experiment after mixing of reactants (Alizarin Dye and Aluminum ion) that passes through manifold unit giving continuous response; this indicates non-existence of dispersion effect by convection or diffusion. This measurement represents (H^o).While the second experiment includes injecting different concentration of (60 and 100 ppm) Al ion concentration for FIA. The obtained value from this experiment represents intensity response for sample injected (H_{max}). The equation used to calculate dispersion (D) is: $D = \frac{H^\circ}{H_{max}}$. As in table 10, these values fall in limit state of dispersion [22,23,24].

Table 10: Determination of dispersion of Al (III) in FIA method

Al(III)concentration (ppm)	Response mm		Dispersion $D = \frac{H^\circ}{H_{max}}$	Mean D
	H^o with dispersion	H_{max} without dispersion		
60	5.99	2.92	2.05	1.95
100	6.53	3.52	1.85	

Interference

Study overlapping some anion and cation with Aluminum ion in the composition of the Aluminum complex at wavelength 494 nm, where the peak height of the complex Aluminum was 2.51 mm when the concentration of Aluminum ion in the complex is (20 ppm) the anion and cation is not interference with Aluminum ion: (

were interference with Aluminum ion, the result shown in table 11.

Table (11) interference some cation with complex Aluminum (III)

No	Ion	Conc.ppm	Peak height mm	Difference	treatment with masking agent
1	**Al^{3+}**	**20**	**2.51**	**———**	**———————————**
2	**Cu^{1+}**	**20**	**2.57**	**0.07**	drop of 100 ppm concentration of NH_3
		100	**2.57**	**0.07**	Two drops of 100 ppm concentration of NH_3
3	**Zn^{2+}**	**20**	**2.76**	**0.25**	drop of 100 ppm concentration of NH_3
		100	**2.79**	**0.28**	Two drops of 100 ppm concentration of NH_3
4	**Fe^{3+}**	**20**	**2.82**	**0.31**	drop of 100 ppm concentration of KH_2PO_4
		100	**2.88**	**0.37**	Two drops of 100 ppm concentration of NH_3

Applications

In FIA system preparing 60 ppm of Pharmaceutical Sample and Aqueous solution found that the average height of the top of the curve is equal to 2.92 mm, which is equivalent to 60 ppm as well as it was the application of the same work for the FIA system, the result show in table 12.

Table 12: Applications of determinate Al(III) in Pharmaceutical Sample and aqueous solution by FIA.

No	Sample	Take value- ppm	found value- ppm	Recovery%
1	Ballox plus	30	29.59	98.64
2	Arkalox plus	30	2979	99.3
3	Malaous	30	30.1	100.33
4	Moxal	30	29.49	98.3
5	Aqueous solution	30	29.59	98.64

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