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New Design of Flow Injection Unit for Determination of Aluminum (Iii) by Alizarin Dye

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ABSTRACT

A new simple and rapid method was reported for the accurate and precised spectrophotometric determination of Aluminum [Al (III)] using flow injection analysis (FIA). The method is based on determination of Al (III) by Alizarin dye spectrophotometrically at 494nm.The variousphysical and chemical parameters affecting on determination of Al have been investigated including flow rate, reaction coil length, and volume of reagent (Alizarin), volume of sample, pH,and concentration of both reactants.The precision and accuracy of the results were determined through reproducibility. The interferences of ions were also checked using different ions. The method allows the determination of linear range (2-140) mg/l and the sampling rate of 120 samples 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). The applications of this method were also studied for some pharmaceutical samples. Dispersion coefficient is measured for the method.

Keywords: flow injection analysis, alizarin dye, aluminum(iii), reproducibility.

1. INTRODUCTION

Flow injection analysis (FIA) is 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[1.] Ruzicka and Hansen[2] conceived the pioneerin 1975 and still largely use flow injection analysis (FIA).Conventional FIA analyzers designed as closed and dedicated systems are useful to work with very well defined sample compositions [3] .In 1990 Ruzicka and Marshall[4] developed (FIA) 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. 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, highly efficient, fast, distinct and sensitive to chemical analyses and the number of modeling large and limits of detection of low-lying[7]. Anthraquinone derivatives are one of the promising indicators for low-polar solvents and in general known as analytical reagents. Alizarin (1,2-dihydroxy-9,10-anthraquinone) is applied in chemical analysis as well. The absorption maximum of the neutral non-dissociated form is located at 430 nm[8-15] .Aluminumis 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 spectrophotometric determination of aluminum bybromooxine, pyridylazoresorcinol (PAR), 1-(2-pyridylazo)-2-naphtol (PAN) have been used. But, these reagents are less sensitive ($\varepsilon = 8.8\times10^3$, 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 been synthesized in this investigation 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].The aim of this study is the determination aluminum (III) by alizarin dyethrough a new design of flow injection unit.

2. MATERIALS AND METHODS

2.1 *Instrumentation*

Analytical Balance sensitive Denver Instrument, Spectrophotometer LabomedinG single beam, USA, and Shimadzu UV-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.

2.2 *Preparation of Solutions*

1-A stock solution of 2000 mg/l or ppm of Aluminum ion was prepared by dissolving requisite amount of $[Al_2(SO_4)_3.18H_2O]$in distilled water adding 1ml of H_2SO_4 Conc., and then other solutions were prepared using dilution law.

2- 0.001 M of Alizarin Dye was prepared by dissolving (0.0240 g) of Alizarin Dye in 50 mL of distilled Alcohol and then transferred to 100 ml volumetric flask. The volume was made up to the mark with distilled water.

3- A buffer solution of pH 7 was prepared by using 0.1M Sodium Carbonate and 0.2M hydrochloric acid. For0.1M Sodium Carbonate, 2.5g of Sodium Carbonate was dissolved in distilled water and transferred to 250 ml volumetric flask. 0.2 M hydrochloric acid was prepared by diluting HCl conc. having S. G (1.8) and purity (36-37.5)%. After preparation of solution standardization was performed against carbonate solution[18].

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3. RESULT AND DISCUSSION

3.1 *Determination of maximum wavelength*

Maximum absorption for the dye and the complex of Al(III) with dye were first determined by using ultraviolet visible spectroscopy and then reaction conditions are optimized for the complex formation. In this study λ_{max} of dye and complex were found to be 432 nm and 494 nm respectively as shown in Fig .1.

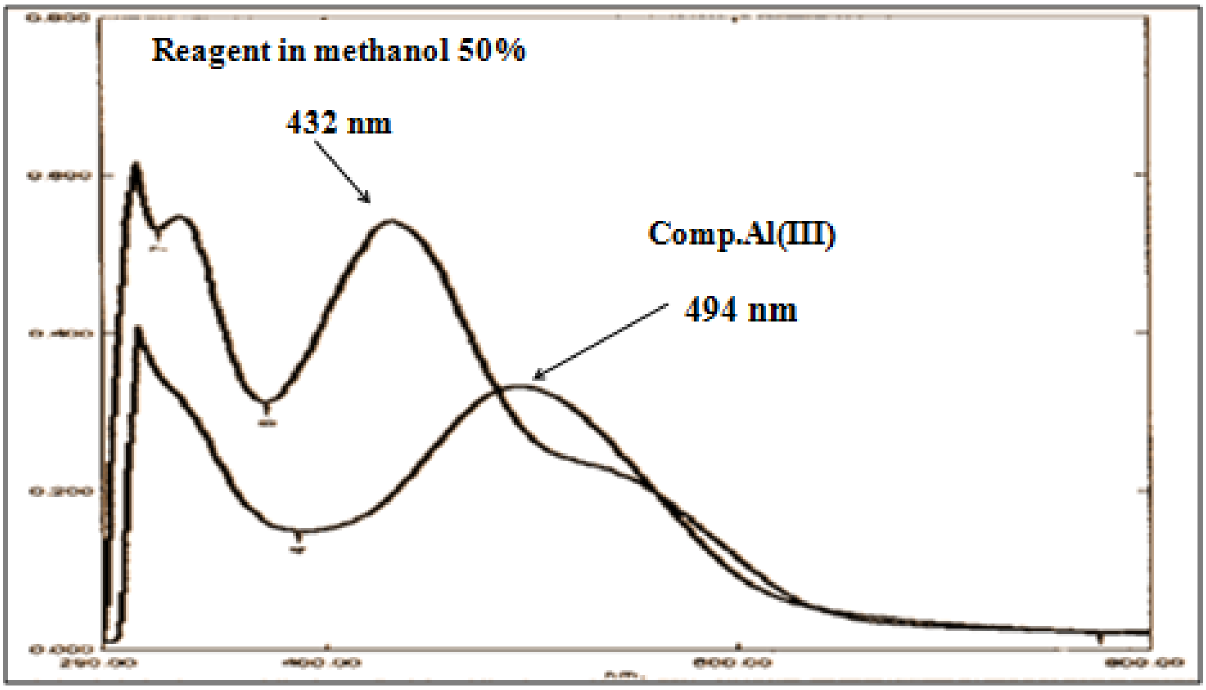

Fig.1: UV-Vis spectra for Aluminum complex and reagent (dye)

3.2 *The design Flow injection unit*

The typical design of Flow Injection unit for the determination of Al ion is shown as Fig .2.

To find out the best solvent for the reagent, different solvents and varying compositions were made and their peak heights were determined. Following observations are obtained:

1- The peak height of the reagent dissolved in ethanol was found to be 8.68mm

2- The peak height of the reagent dissolved in methanol was found to be 5.04 mm.

3- The peak height of the reagent dissolved in methanol and water (1:1) was found to be 2.11 mm.

The above measurements showed that the best signal is when the solvent is methanol and water in a ratio of 1:1.This gives peak shape and has less peak height than other solvents.

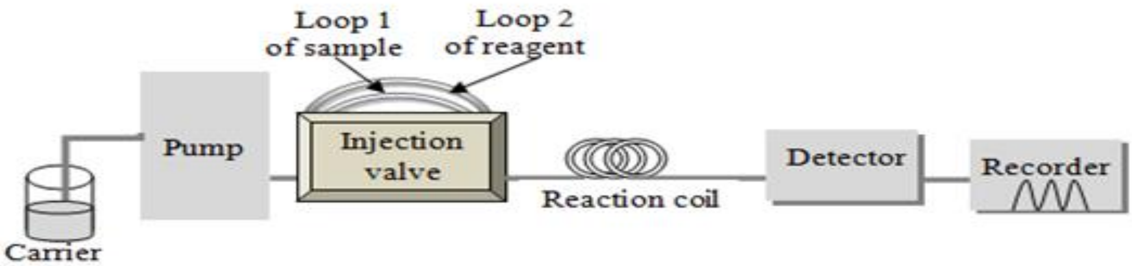

Fig.2: New design of FIA at: flow rate=9.0ml min^{-1},reaction coil length =50cm, [Al (III)] =20ppm,[Alizarin] =0.001M

3.3 *Physical Parameters*

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.

3.3.1 *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, reaction coil length = 30 cm, [Alizarin] =0.001M, and sample loop (L_1) = reagent loop (L_2) =30cm

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

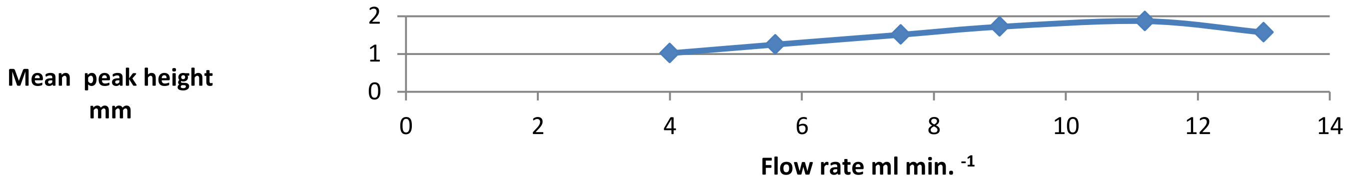

Fig.3: Change in peak height with flow rate

3.3.2 *Effect of the reaction coil length*

Table 2 and fig. 4shows the effect of reaction coil length on the peak height in the range (20-70) cm, it was seen that the suitable reaction coil length is 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

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

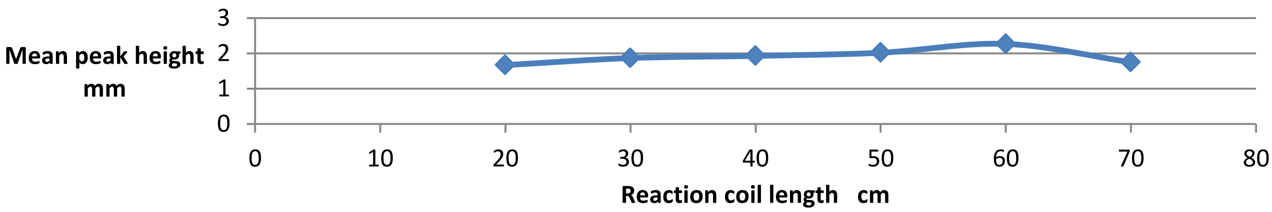

Fig.4: Change in peak height with the Reaction coil length

3.3.3 *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 (table 3 and fig.5). The peak height increased to the maximum at 235.5 µL and then decreased. Therefore, this volume i.e. 235.5µL was chosen for further work.

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**

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

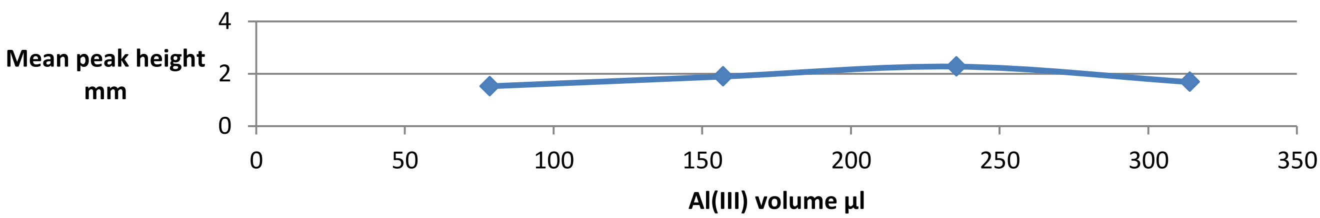

Fig.5: Change in peak height with sample volume

3.3.4 *Effect of Alizarin dye volume*

The influence of the various volume of Alizarin was studied in the range (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 shown by 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

No	Alizarin volume 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

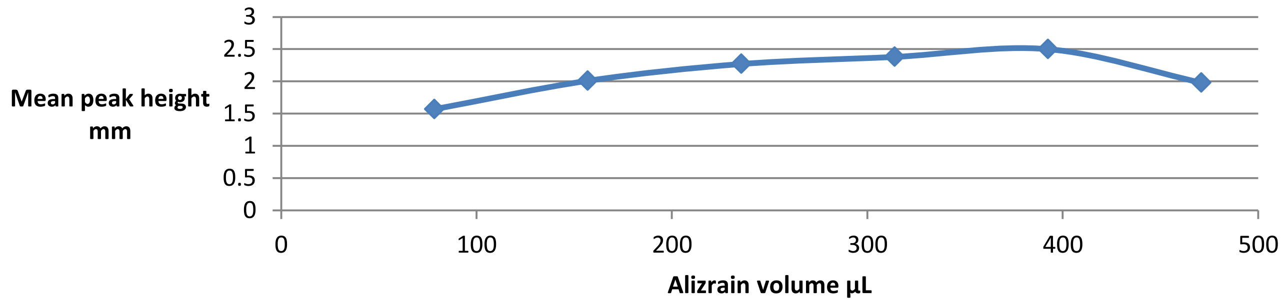

Fig.6: Change the peak height with the Alizarin dye volume

3.4 *Chemical Parameters*

3.4.1 *Effect of pH*

The effect of pH upon the formation of the complex was investigated in the range from (3-8). The optimum pH was found to be [6-7] as evident from table 5 and fig.7. Therefore, a suitable buffer from Hydrochloric acid (HCl) and Sodium Carbonate (Na_2CO_3) was prepared to adjust the pH of medium.

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.

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

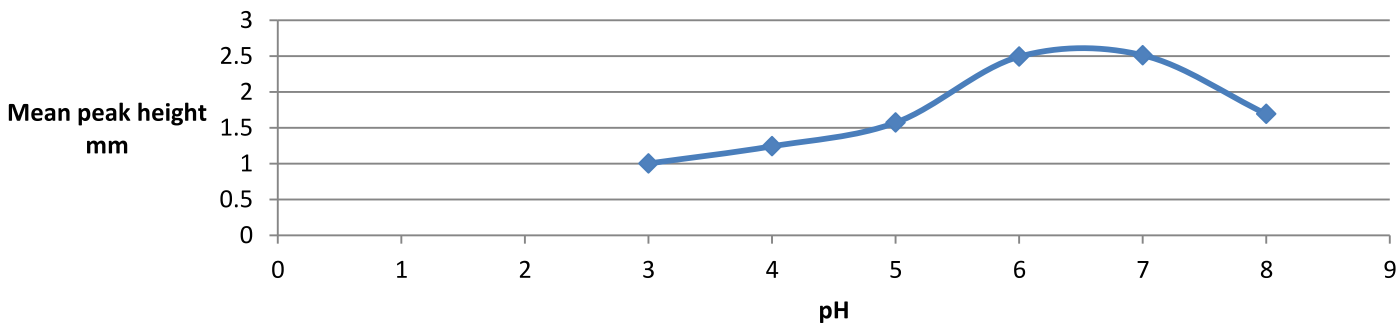

Fig.7: Change the peak height with pH

3.4.2 *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. 8 shows the effect of reagent concentration on the peak height of the Al (III). The maximum peak height was obtained with $1x10^{-3}$ M reagent, therefore this concentration of reagent was chosen for further work. At $1x10^{-2}$ M double peak appear as compare to this chosen 1×10^{-3}M as best concentration.

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 $^{-1}$

No	Reagent Con. Mol/l	Peak	Height	mm	Mean	S.D	RSD%
1	$1x10^{-8}$	0.85	0.85	0.86	0.85	0.01	1.07
2	$1x10^{-8}$	1.13	1.13	1.14	1.13	0.01	0.88
3	$1x10^{-8}$	1.17	1.18	1.16	1.17	0.01	0.85
4	$1x10^{-8}$	1.30	1.30	1.30	1.30	0.00	0.00
5	$1x10^{-8}$	2.17	2.20	2.20	2.19	0.02	0.91
6	$1x10^{-8}$	2.51	2.51	2.51	2.51	0.00	0.00
7	$1x10^{-8}$	2.60	2.60	2.60	2.60	Double Peak	

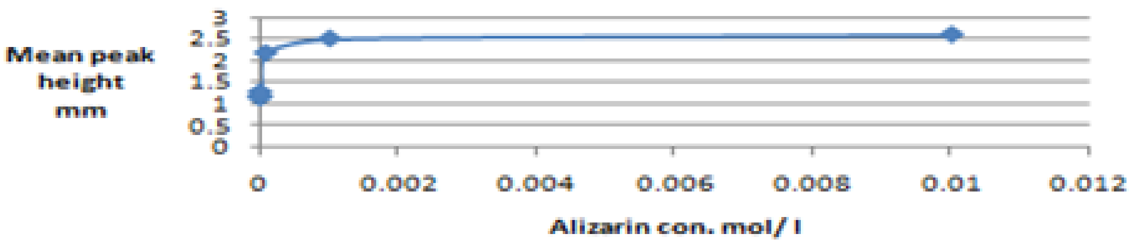

Fig.8: Change in peak height with reagent concentration

3.4.3 *The effect of the composition of the solvent*

The effect of solvent composition was studied in the range of (75%-30%) of methanol-water to dissolve the dye . Table 7 and fig 9 show 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

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

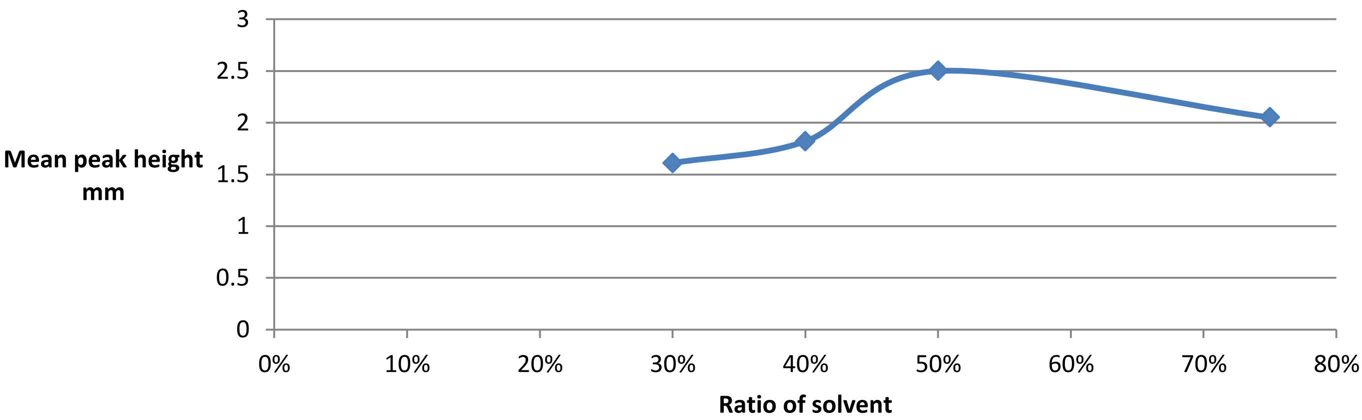

Fig.9: Change in peak height with Ratio of solvent

4. CALIBRATION CURVE IN FIA METHOD

Calibration curve was prepared at the optimum conditions of complexation and change through the metal ion concentration, the results are shown in table 8 and fig. 10.The calibration curve is linear in the range of 2 -140 mg l^{-1}. The slope = 0.0126 and Correlation coefficient R^2 = 0.997.

Table-8: Effect of Al (III) concentration 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=2.21m

No.	[Al(III)] 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

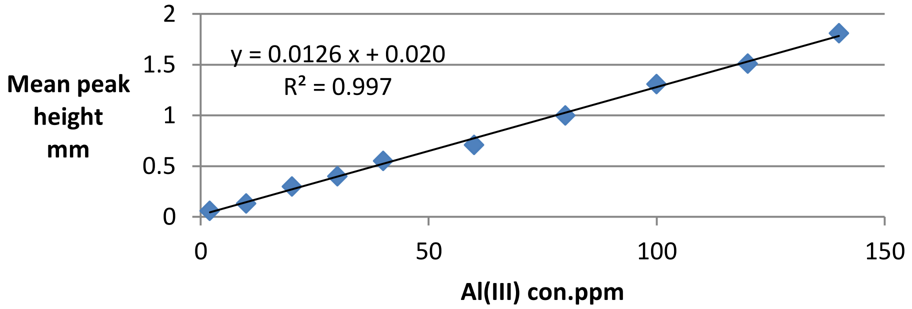

Fig.10: Calibration curve of Al (III) in FIA method

5. REPRODUCIBILITY

The precision range and effectiveness of method used in the determination of Aluminum (III) was studied through reproducibility. For this purpose 60 ppm of sample was injected and the peak height was measured ten times. The values of standard deviation (0.008) and relative standard deviation (0.274%) clearly reveals the accuracy and effectiveness of system for determination the ion. The results are shown in table 9 and fig. 11.
From the results of Reproducibility study, the detection limit was calculated by using (D.L= (3×con.×S.D.)/ mean) and was found to be 0.5mg / l .

Table-9: Reproducibility for 60ppm of Al (III)

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

6. 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 mixture of reactants (Alizarin Dye and Aluminum ion) passed through manifold unit giving continuous response; this indicates non-existence of dispersion effect by convection or diffusion. This measurement is represented by (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 [22-24]

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

[Al(III)] (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	

7. INTERFERENCE

Study of overlapping some anions and cations with Aluminum ion in the composition of the Aluminum complex at wavelength 494 nm was performed, where the peak height of the complex was 2.51 mm. When the concentration of Aluminum ion in the complex was (20 ppm) the anions and cations including Na^{+} ,Ca^{2+} ,Ni^{2+} ,Pb^{2+}, NO_3^{-}, K^{+},Mg^{2+},CH_3COO^{-} ,SO_4^{2-}, PO_3^{3-},Cl^{-}) showed no interference with Aluminum ion, but Cu^{2+}, Zn^{2+} and Fe^{3+} were interfered with Aluminum ion shown in table 11.

Table-11: Interference of some cations with complex of Aluminum (III

No.	Ion	[Cation] 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 NH_3
		100	2.57	0.07	Two drops of 100 ppm NH_3
3	Zn^{2+}	20	2.76	0.25	drop of 100 ppm NH_3
		100	2.79	0.28	Two drops of 100 ppm NH_3
4	Fe^{3+}	20	2.82	0.31	drop of 100 ppm KH_2PO_4
		100	2.88	0.37	Two drops of 100 ppm NH_3

8. APPLICATIONS

The proposed method was applied for the determination of Aluminum ion in Pharmaceutical Sample and aqueous solution, the recoveries of known concentrations of Aluminum ion in these samples were investigated. Table 12 shows the results of the recovery.

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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