

# SIMPLE FLOW INJECTION ANALYSIS SYSTEM FOR THE TURBIDIMETRIC DETERMINATION OF CHROMIUM(III) ION WITH MEFENAMIC ACID USING AYAH6SX1-ST-2D SOLAR CELL CFIA

Nagam S. Turkie Al-Awadie , Mustafa K. Kadhim Al-saeedi\*

Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.

## ABSTRACT

A new turbidimetric-flow injection method is described for the determination of chromium(III) ion in pure formulation. The method is characterized by simplicity, sensitivity and fast, it is based on formation of ion pair compound between chromium(III) ion and mefenamic acid (MFA) in an aqueous medium for the formation of yellowish green precipitate. This precipitate was determined using homemade Ayah 6SX1-ST-2D Solar cell CFI Analyser. Optimum concentrations of chemical reactants, physical instrumental conditions have been investigated. The linear dynamic range of chromium(III) ion was 0.6-10 mMol.L<sup>-1</sup> while correlation coefficient (r) was 0.9956 and percentage linearity (%r<sup>2</sup>) was 99.13%. Limit of detection was 15.46 µg/sample from the stepwise dilution of minimum concentration for the lowest concentration in the linear dynamic range of the calibration graph with R.S.D% (n=5,8) < 0.2% for concentration 1 and 9 mMol.L<sup>-1</sup> respectively of chromium(III) ion. The method was applied successfully for the determination of chromium(III) ion in pure formulation. A comparison was made between the mean of pure formulation with the theoretical value via the use of paired t-test. It shows that there were no significant difference between the means for pure formulation and theoretical value in development method and significant difference between the means for pure formulation and theoretical value in classical method.

**Keywords:** Chromium(III) ion, Flow injection analysis, Turbidity.

## INTRODUCTION

Chromium is a chemical element with symbol Cr and atomic number 24. It is the first element in Group 6. Chromium is one of the most widely distributed heavy metals in the earth's crust. It is normally found in two stable oxidation states i.e. Cr(III) ion and Cr(VI). Chromium is required in small quantities as an essential trace metal, nutrient and its deficiency may result in several physiological disorders. Most of the biological tissues contain Cr(III) ion which is usually nontoxic, whereas Cr(VI) ion is highly toxic to the organisms. It is known that an increase in the content of this element in soils makes them infertile and that the toxic effect depends to some extent on the oxidation state of chromium<sup>1</sup>. Chromium is available as silvery metallic appearance, solid phase, 1907 °C melting point and 7.19 g/cm<sup>3</sup> density<sup>2</sup>. There are many sensitive techniques for chromium determination, such as ICP-MS<sup>3-5</sup>, ICP-AES<sup>6</sup>, HPLC<sup>7</sup>, spectrophotometry<sup>8,9</sup>.

The purpose of this work is to describe a simple, precise and sensitive flow injection turbidimetric method with the use of Ayah 6SX1-ST-2D Solar cell CFI Analyser for the determination of Cr (III) ion in pure formulations. The method based on the formation of yellowish green precipitate as an ion-pair compound by mefenamic acid with Cr (III) ion in aqueous medium. The turbidimetry is measured via reflection of incident light from the surfaces of precipitate particles at 0-180°. The positive signal from reflection recorded by Ayah 6SX1-ST-2D Solar cell supplied with linear array of six snow-white light emitting diode as a source and two solar cells as a detector.

## EXPERIMENTAL

### REAGENTS AND CHEMICALS

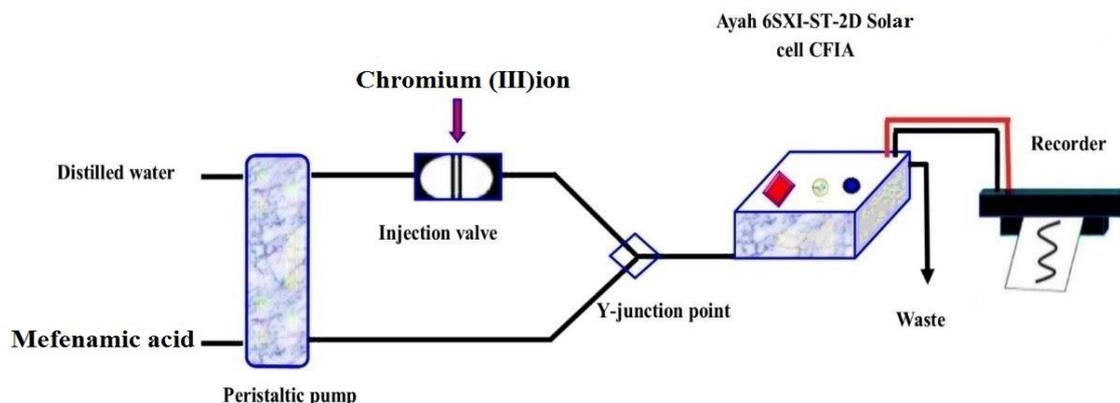
All chemicals used were of analytical-reagent grade and distilled water used to prepare the solutions. A standard solution ( $0.1 \text{ Mol.L}^{-1}$ ) of Cr (III) ion was prepared by dissolving 2.6648 g of chromium chloride hexahydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $266.48 \text{ g.mol}^{-1}$ , BDH) in 100 mL of distilled water. A stock solution ( $0.1 \text{ Mol.L}^{-1}$ ) of mefenamic acid ( $\text{C}_{15}\text{H}_{15}\text{NO}_2$ ,  $241 \text{ g.mol}^{-1}$ , SDI) was prepared by dissolving 2.41 g in 100 mL of  $0.1 \text{ Mol.L}^{-1}$  NaOH.  $0.1 \text{ Mol.L}^{-1}$  of Sodium hydroxide solution (NaOH,  $40 \text{ g.mol}^{-1}$ , BDH) was prepared by dissolving 0.4 g in 100 mL distilled water (Standardized with HCl solution which in turn to calibrate against  $0.1 \text{ Mol.L}^{-1}$  sodium carbonate ( $\text{Na}_2\text{CO}_3$ ,  $105.99 \text{ g.mol}^{-1}$ , BDH)).

### Sample Preparation

0.5199 g of (Chromium (III) nitrate nonahydrate, sigma aldirch) was weighed and dissolved in 100 mL of distilled water to obtain concentration equivalent to  $100 \text{ mMol.L}^{-1}$  of sample.

### Apparatus

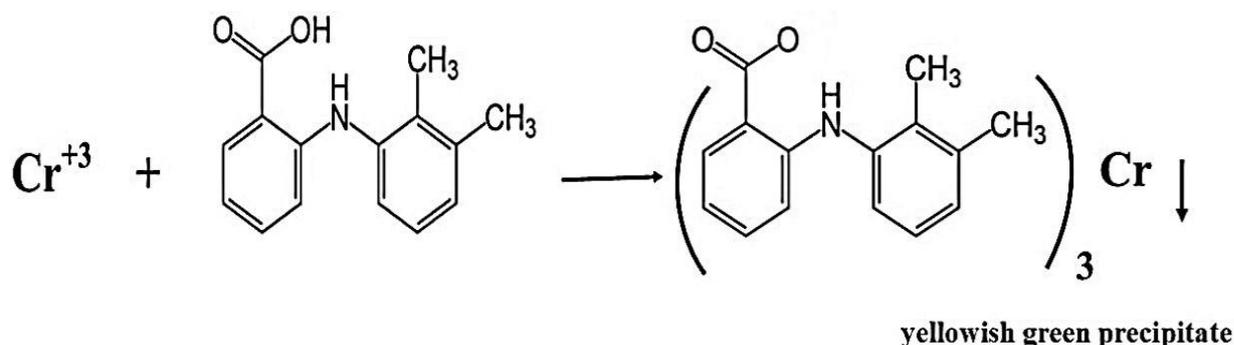
The flow system used for the determination of Cr (III) ion is shown schematically in **Figure 1**, Peristaltic pump – 2 channels variable speed (Ismatec, Switzerland), Injection valve with valve 6-port medium pressure (IDEX corporation, USA) with sample loop ( $0.75 \text{ mm i.d. Teflon}$ , different length). The response was measured by a homemade Ayah 6SX1-ST-2D Solar cell CFI Analyser, which used a six snow-white light emitting diode LEDs for irradiation of the flow cell at 2 mm path length. Two solar cells are used as detector for collecting signals via sample travel for 60 mm length. The readout of the system composed of x-t potentiometric recorder (Kompenso Graph C-1032) Siemens (Germany), this recorder measured by (1-500) mV or voltage and digital AVO-meter (auto range) (0-2 volt) (China). UV-Vis spectrophotometer single beam type PU 8720, Philips, Japan was used to scan the spectrum of Cr (III) ion using 1 cm quartz cell.



**Fig. 1: Flow diagram manifold system used for the determination of Cr (III) ion**

### Methodology

The flow system consisting of two lines was used for the determination of Cr (III) ion by the reaction between Cr (III) ion and mefenamic acid ( $3 \text{ mMol.L}^{-1}$ ) in aqueous medium to form a yellowish green color precipitate as an ion pair complex form. The first line represents the carrier stream (Distilled water) at  $1.7 \text{ mL.min}^{-1}$  flow rate which leads to the injection valve to carry Cr (III) ion, sample volume  $145 \mu\text{L}$ ; while the second line supplies mefenamic acid solution at  $2.1 \text{ mL.min}^{-1}$ . Both lines meet at a Y-junction, with an outlet for reactants product from complex, which passes through a homemade Ayah 6SX1-ST-2D solar cell CFI Analyser that works with six snow white light emitting diodes LEDs used as a source. Each solution injected was assayed in three times. The response profile of which was recorded on x-t potentiometric recorder to measure energy transducer response expressed as average peak height in mV by reflection of incident light at  $0-180^\circ$ . A probable mechanism of ion pair formation for Cr (III) ion- mefenamic acid system is represented in **scheme 1**.



Scheme. 1: Proposed mechanism of reaction between Cr (III) ion and mefenamic acid

## RESULT AND DISCUSSION

### Study of optimum parameter

The flow injection manifold as shown in **Figure 1** was used for studying of chemical and physical parameters, in order to obtain the optimum conditions for the system. These variables were optimized by making all variables constant and varying one each at time.

### Chemical Variables

#### Mefenamic acid Concentration

Using different concentration of mefenamic acid (0.3-9) mMol.L<sup>-1</sup>. A 9mMol.L<sup>-1</sup> of Cr(III) ion was injected through the carrier stream (distilled water) with 122μL sample volume at a flow rate 1.3, 1.7 mL.min<sup>-1</sup> for carrier stream and reagent respectively. 1.9 V, the applied voltage to the LEDs. Each measurement was repeated for three times. **Figure 2 A** shows the response profile for this study, **Figure 2 B** indicate, the variation of energy transducer response with variation of MFA concentration using Ayah 6SX1-ST-2D solar cell -CFI Analyser. It was noticed that an increase of response height of precipitate species with increase of concentration of mefenamic acid up to 3 mMol.L<sup>-1</sup>, while at higher concentration (> 3mMol.L<sup>-1</sup>) lead to decrease of response height. It really might be attributed to increase of the density of the precipitate colored product which prevent the light of LEDs to arrival to the detector (twin solar cell). Therefore 3 mMol.L<sup>-1</sup> of mefenamic acid was regarded as the optimum concentration for the determination of Cr(III) ion, that used for the further work. The results were summarized in **Table 1**.

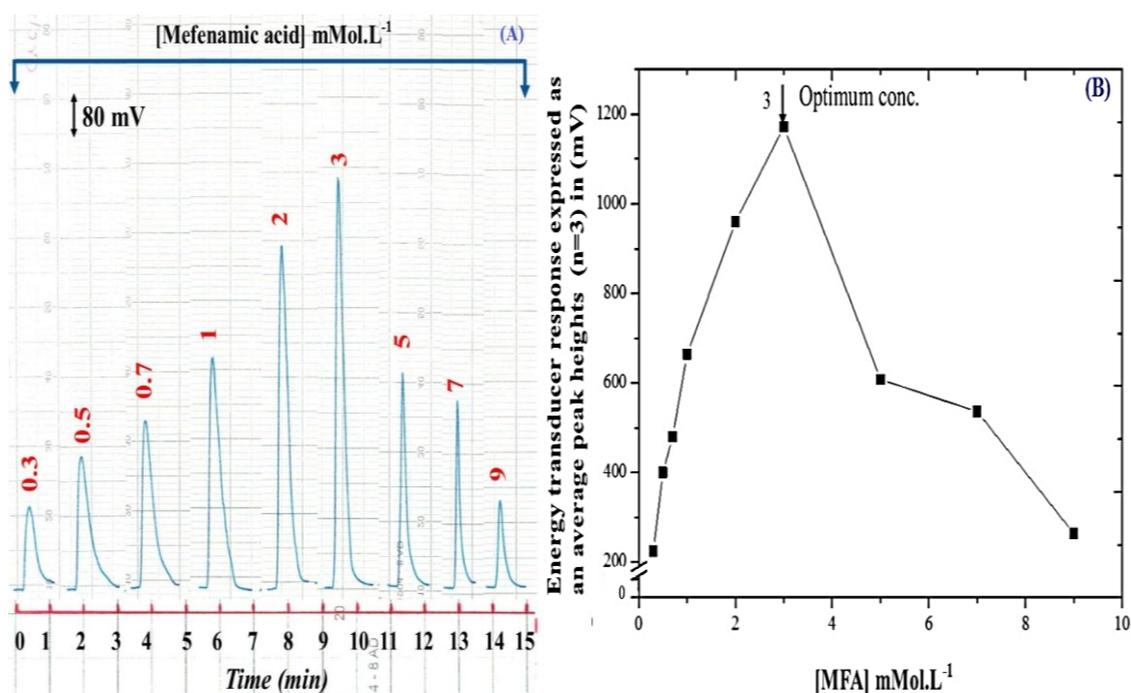


Fig. 2: Effect of [MFA] on:  
 (A): Profile versus time using different concentration of MFA.  
 (B): Energy transducer response in mV for Cr(III) ion-MFA system.

Table 1: Effect of MFA concentration on the measurement of energy transducer response via reflection of incident light of LEDs for the determination of Cr(III)ion

[MFA] mMol.L <sup>-1</sup>	Energy transducer response expressed as an average peak heights (n=3) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$
0.3	224	0.10	224 ± 0.556
0.5	400	0.06	400 ± 0.596
0.7	480	0.04	480 ± 0.477
1	664	0.05	664 ± 0.825
2	960	0.04	960 ± 0.954
3	1172	0.03	1172 ± 0.873
5	608	0.08	608 ± 1.208
7	536	0.10	536 ± 1.332
9	264	0.10	264 ± 0.656

### Effect of basic medium as a carrier stream on the output of responses

The effect of NaOH on the precipitation of Cr(III)ion was studied using 9 mMol.L<sup>-1</sup> of Cr(III)ion . In the previous section achieved , 3 mMol.L<sup>-1</sup> of mefenamic acid was used as the precipitate agent . Different concentrations of NaOH (5-90 mMol.L<sup>-1</sup>) were prepared as a carrier stream for the Cr(III)ion, in addition to the use of distilled water as a carrier stream , 122  $\mu$ L of sample volume at 1.3, 1.7 mL.min<sup>-1</sup> flow rate of carrier stream and reagent respectively . **Figure 3A,B** shows the decrease of peak height with increase of NaOH concentration . It might be attributed that an increase in the basic concentration of the medium leads to precipitation of Cr(III)ion as a hydroxides previous to precipitate with mefenamic acid . Therefore, the neutral medium (distilled water) was selected as the optimum medium for system (Cr(III)ion – MFA system). The obtained results are tabulated in **Table 2**.

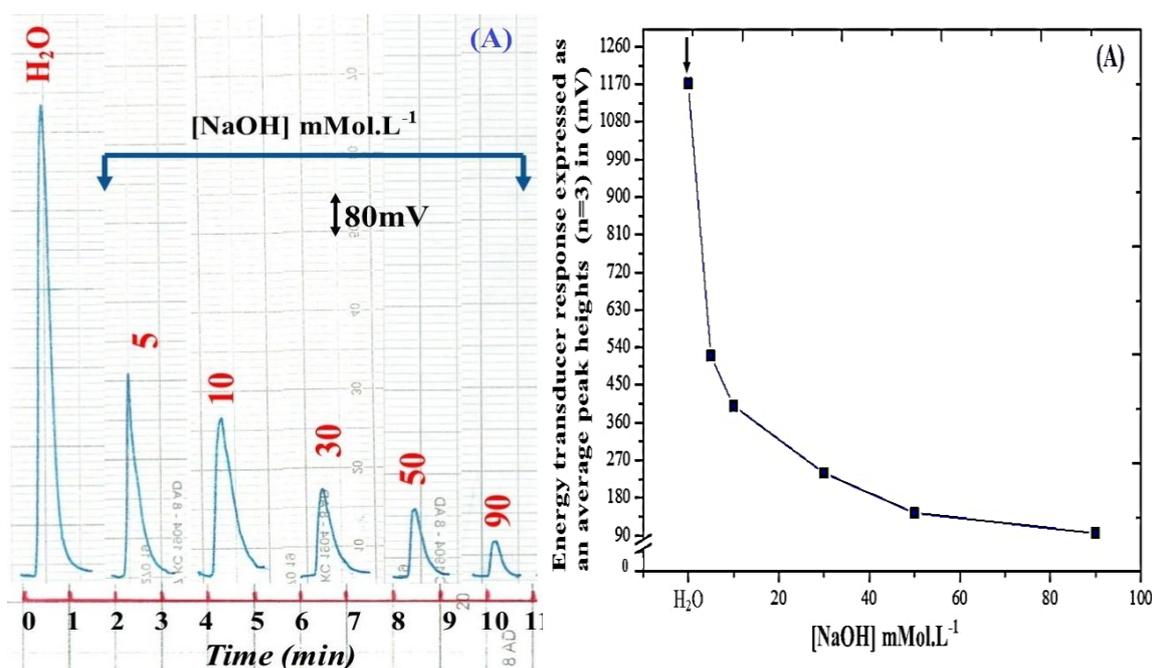


Fig. 3: Variation of concentration of basic medium as a carrier stream on:  
(A): Response profile using Ayah 6SX1-ST-2D solar cell CFIA, for determination of Cr(III)ion  
(B): Transducer energy response (mV)

Table 2: Variation of NaOH concentration as a carrier stream on the energy transducer response of Cr(III)ion – MFA system

[NaOH] mMol.L <sup>-1</sup>	Energy transducer response expressed as an average peak heights (n=3) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$
H <sub>2</sub> O	1172	0.03	1172 ± 0.873
5	520	0.06	520 ± 0.775
10	400	0.07	400 ± 0.696
30	240	0.10	240 ± 0.596
50	144	0.13	144 ± 0.465
90	96	0.14	96 ± 0.334

## Physical Variables

### Flow rate

Using optimum concentration of the MFA (3 mMol.L<sup>-1</sup>) with Cr(III)ion (9 mMol.L<sup>-1</sup>), a set of experiments were conducted for the optimization of the preferred flow rate 0.3-2.6 mL.min<sup>-1</sup> for carrier stream (distilled water) and 0.4-3.4 mL.min<sup>-1</sup> for reagent (mefenamic acid). Applied voltage to the light emitting diodes (six snow white) was 1.9 V with 122 μL injected volume for Cr(III)ion. It was noticed that at slow flow rate there was an increase in dispersion due to diffusion, which in turn to cause an increase in particle size leading to destruction of the flow of liquids, which causes broadening, distorted, irregular of responses profile (Figure 4A,B), (i.e. 0.3 mL.min<sup>-1</sup>) and increase in peak base width ( $\Delta t_B$ ), while at higher flow rate (i.e. >0.9, 1.3 mL.min<sup>-1</sup>) for carrier stream and reagent respectively there was an increase in peak height up to 1.7 & 2.1 mL.min<sup>-1</sup> followed by slightly increase and then constant; this might be due to departure speed of precipitate particles from measuring cell at a short time, So; the best flow rate for the completion for Cr(III)ion-MFA system was 1.7 and 2.1 mL.min<sup>-1</sup> for carrier stream and reagent to obtain regular response, sharp maxima and less the consumption of reactant solutions. All results were summarized in Table 3.

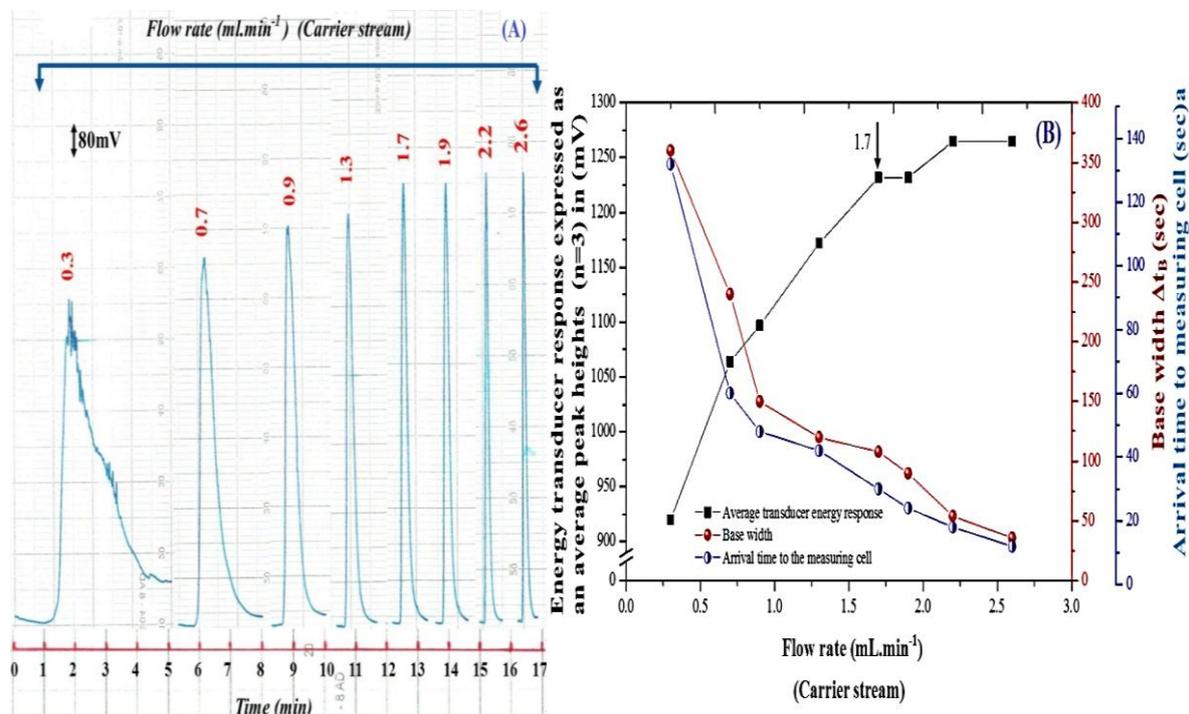


Fig. 4: Effect of the variation of flow rate on:

(A): Profile versus time

(B): Variation of energy transducer response, Base width and Departure time for sample segment from injection valve to the measuring cell.

**Table 3: Effect of variable flow rate on the measuring of energy transducer response via reflection of incident light for determination of Cr(III)ion (9 mMol.L<sup>-1</sup>)-[MFA]system using 122 μL sample volume**

Peristaltic Pump speed	flow rate mL.min <sup>-1</sup>		Energy transducer response expressed as an average peak heights (n=3) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$	Base width $\Delta t_B$ (sec)	$t^*$ (sec)	V* (mL)	C* (mMol.L <sup>-1</sup> )
	Line 1	Line 2							
5	0.3	0.4	920	0.02	920 ± 0.457	360	132	4.322	0.254
10	0.7	0.8	1064	0.02	1064 ± 0.529	240	60	6.122	0.179
15	0.9	1.3	1068	0.02	1068 ± 0.531	150	48	5.622	0.195
20	1.3	1.7	1172	0.03	1172 ± 0.873	120	42	6.122	0.179
25	1.7	2.1	1232	0.03	1232 ± 0.918	108	30	6.962	0.158
30	1.9	2.6	1232	0.03	1232 ± 0.918	90	24	6.872	0.160
35	2.2	2.8	1265	0.03	1265 ± 0.943	54	18	4.622	0.238
40	2.6	3.4	1265	0.03	1265 ± 0.943	36	12	3.722	0.295

$\Delta t_B$  : Base width of response

$t^*$  = Departure time for sample segment from injection valve to the measuring cell

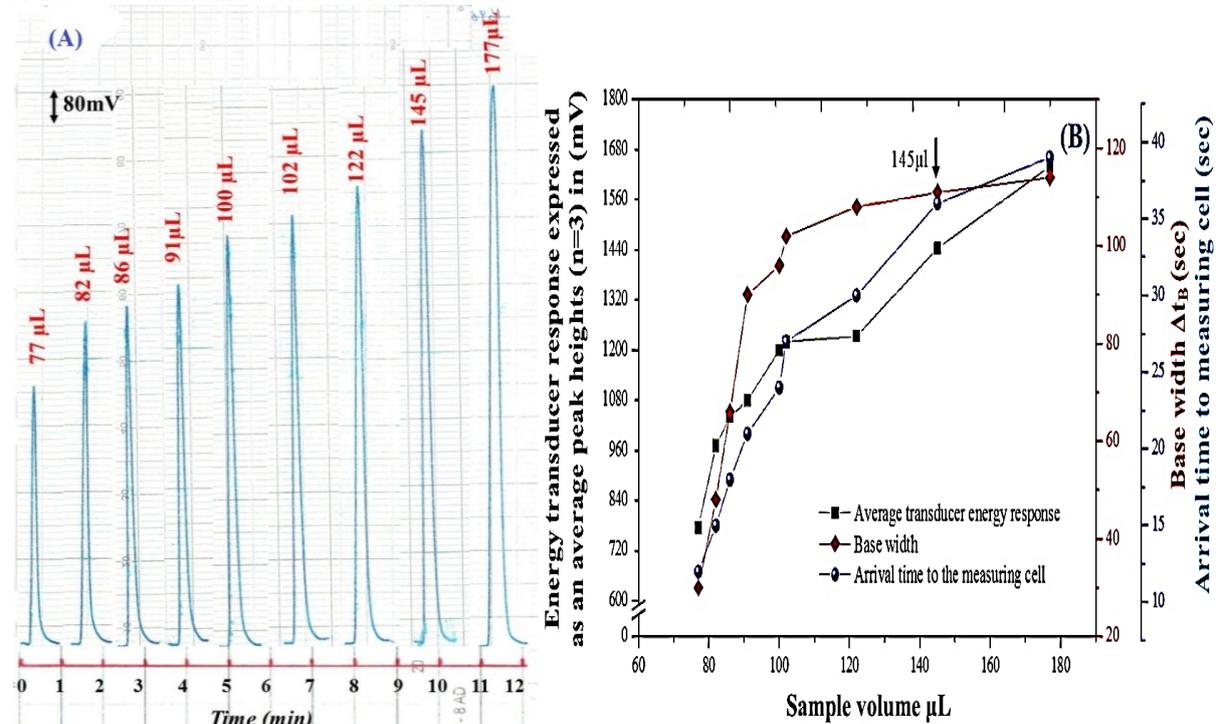
V\*= Volume of segment at flow cell

C\*= Concentration of segment at flow cell

Line 1: Carrier stream , Line 2: precipitate agent (reagent) .

**Effect of sample volume**

The effect of sample volume was studied using Cr(III)ion (9 mMol.L<sup>-1</sup>) –MFA (3 mMol.L<sup>-1</sup>) system , 1.7 and 2.1 mL.min<sup>-1</sup> flow rate for carrier stream and MFA line respectively and 1.9 volt DC applied voltage to the light sources . Variable injected volume of sample was studied in the range 77-177 μL by changing the length of the sample loop in the injection valve. From **Figure 5 A,B**, it was notice that an increase in the sample volume led to a significant increase in sensitivity ,more perceptible than low volumes. At the same time , base width ( $\Delta t_B$ ) of response is increase (i.e. increase analysis time) with increase sample volume .Therefore: 145 μL was chosen as the optimum sample volume for Cr(III)ion to obtain regular response , sharp maxima peak and less consumption of chemical solutions .**Table 4** summarized the results obtained.



**Figure 5: Effect of the variation of sample volume on:**  
**(A): Profile versus time**  
**(B):Variation of energy transducer response using optimum parameters**

**Table 4: Effect of the variation of sample volume on the energy transducer response for the determination of Cr(III)ion using Ayah 6XS1-ST-2D Solar cell CFIA**

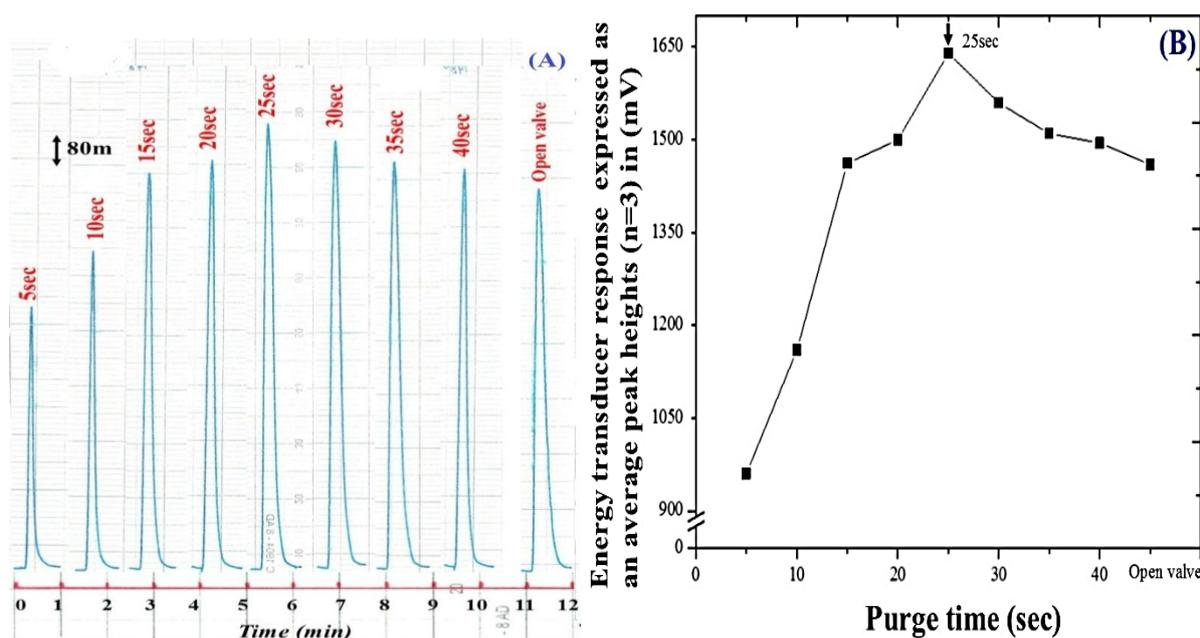
Sample volume $\mu\text{L}$	Energy transducer response expressed as an average peak heights ( $n=3$ ) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$	Base width $\Delta t_B$ (sec)	$t^*$ (sec)
77	776	0.05	$776 \pm 0.964$	30	12
82	972	0.03	$972 \pm 0.724$	48	15
86	1040	0.05	$1040 \pm 1.292$	66	18
91	1080	0.06	$1080 \pm 1.610$	90	21
100	1200	0.06	$1200 \pm 1.789$	96	24
102	1220	0.06	$1220 \pm 1.819$	102	27
122	1234	0.07	$1234 \pm 2.146$	106	30
145	1444	0.06	$1444 \pm 2.152$	109	36
177	1640	0.06	$1640 \pm 2.445$	115	39

$\Delta t_B$  : Base width of response

$t^*$  = Departure time for sample segment from injection valve to the measuring cell.

### Effect of Purge Time

Using the optimum parameters (sample volume  $145\mu\text{L}$ , flow rate  $1.7\text{mL}\cdot\text{min}^{-1}$  for carrier stream and  $2.1\text{mL}\cdot\text{min}^{-1}$  for reagent ) achieved in previous sections for Cr(III)ion( $9\text{mMol}\cdot\text{L}^{-1}$ )–MFA ( $3\text{mMol}\cdot\text{L}^{-1}$ ) system. A study was carried out to determine the optimum allowed permissible time for the sample segment to be injected from the injection valve. 5-40 seconds were used in this study in addition to the open valve mode. **Figure 6 A,B** shows the continuation of the height output response with increase of purge time up to 25 second after that there was a decrease in peak height .The decrease in response might be attributed to the continuation of the passage of carrier stream through injection valve leading to the obstruction of flow which might cause the slow down of precipitating particles movement in front of the detector. Therefore ; 25sec was chosen as optimum purge time for the departure of the sample segment completely from the injection valve . All results were summarized in **Table 5**.



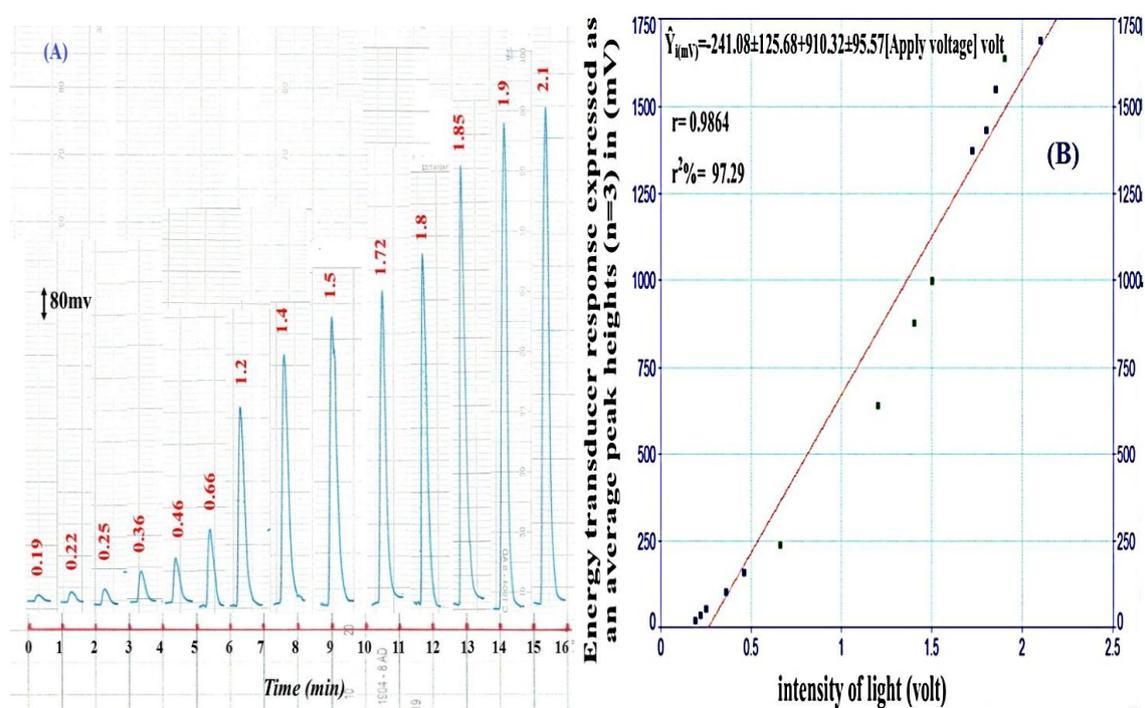
**Fig. 6: Effect of the variation of purge time on:**  
**(A): Response profile (i.e: via reflection of incident light by precipitate species) versus time.**  
**(B): Energy transducer response in (mV) using Cr(III)ion  $9\text{mMol}\cdot\text{L}^{-1}$  –MFA  $3\text{mMol}\cdot\text{L}^{-1}$  system .**

**Table 5: Effect of the variation of purge time on the energy transducer response for the determination of Cr(III)ion using 145  $\mu$ L**

purge time (Sec)	Energy transducer expressed as an average peak heights ( $n=3$ ) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$
5	960	0.11	960 $\pm$ 2.623
10	1160	0.16	1160 $\pm$ 4.611
15	1462	0.23	1462 $\pm$ 8.354
20	1500	0.37	1500 $\pm$ 13.788
25	1640	0.33	1640 $\pm$ 13.445
30	1560	0.19	1560 $\pm$ 7.364
35	1510	0.28	1510 $\pm$ 10.504
40	1495	0.31	1495 $\pm$ 11.514
Open valve	1460	0.22	1460 $\pm$ 7.980

### Incident light intensity

Ayah 6SX1- ST-2D solar cell CFIA is characterized by the capability of variation of incident light. Therefore, variable intensity of light source was used 0.19– 2.1 volt for the determination of Cr(III)ion by variation of light intensity channel in Ayah 6SX1- ST-2D solar cell CFIA operation which where monitored by AVO-meter. The optimum conditions that achieved in previous section was used ; 1.7 mL.min<sup>-1</sup> flow rate for carrier stream (distilled water) and 2.1mL.min<sup>-1</sup> for reagent line , 145  $\mu$ L sample volume , and 25 sec permissible time. **Figure 7 A** shows the response height while **Figure 7 B** showing the relationship between energy transducer response versus applied voltage with correlation coefficient  $r = 0.9864$ . It was notice that an increase in the height of response with increase intensity of light source (LEDs) , so 1.9 volt was selected as the optimum voltage for light emitting diode (six snow white) compared with 2.1 volt to preserved the life of light source . The results were tabulated in **Table 6**.



**Fig. 7: Variation of incident light intensity on:**  
**(A): Response profile for Cr(III)ion-MFA system.**  
**(B): Calibration graph for the variation of applied voltages on the energy transducer response using linear equation**

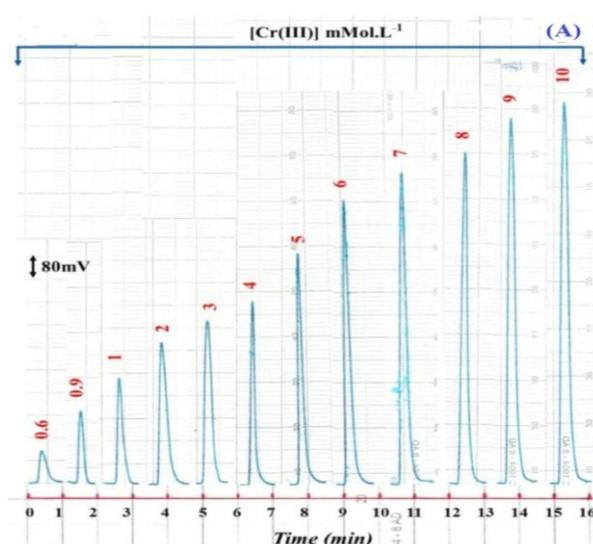
**Table 6: Variation of incident light intensity on transducer energy response**

Intensity of light (Volt)	Energy transducer response expressed as an average peak heights (n=3) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$
0.19	24	0.12	24±0.072
0.22	40	0.13	40±0.129
0.25	56	0.25	56±0.348
0.36	104	0.21	104±0.543
0.46	160	0.61	160±2.425
0.66	240	0.65	240±3.876
1.2	640	0.72	640±11.448
1.4	880	0.04	880±0.874
1.5	1000	0.06	1000±1.491
1.72	1376	0.02	1376±0.684
1.8	1432	0.04	1432±1.423
1.85	1550	0.04	1550±1.540
1.9	1640	0.05	1640±2.037
2.1	1693	0.06	1693±2.524

### Calibration Graph

Using the optimum parameters (chemical and physical) achieved in previous section. A series of solutions of Cr(III) ion (0.4-11) mMol.L<sup>-1</sup> respectively were prepared in order to prepare a scatter plot diagram as shown in **Figure 8 A**. Each measurement was repeated three times. Transducer energy response of Ayah 6SXI-ST-2D solar cell CFI Analyser of the average peak heights (mV) was plotted against the concentration of ion. A straight line graph ranging from (0.6-10) mMol.L<sup>-1</sup> with correlation coefficient (r): 0.9956 as shown in **Figure 8 B**. Above 10 mMol.L<sup>-1</sup> for Cr(III) ion, it was noticed, a broad in the peak height was observed and increase of the base width ( $\Delta t_B$ ) which cause a deviation of correlation coefficient (i.e: deviate from linearity); most probably due to the increase of dense precipitate colored species in front of detector which in turn to accumulation & compactness of particles leading to a large particles and lose of some of the reflecting surface which cause a decrease or constant in the reflection of incident light with increase of concentration of ion.

The UV-Vis spectrophotometric (classical method) at  $\lambda_{max}=357.9$  nm<sup>10,11</sup>. The calibration graph was established to determine of chromium (III) ion from (0.3-14) mMol.L<sup>-1</sup> with correlation coefficient (r): 0.9975 (**Figure 8 C**) with 100  $\mu$ Mol.L<sup>-1</sup> detection limit. The results obtained were tabulated in **Table 7**, including the summary of linear regression for the variation of energy transducer response with [Cr(III)] using first degree equation of the form  $\hat{y}=a\pm s_a t+b\pm s_b t$ <sup>12,13</sup> at optimum conditions. In addition to calculate t-value at 95% confidence level which larger than tabulated t-value indicating clear that the linearity against non linearity is accepted.



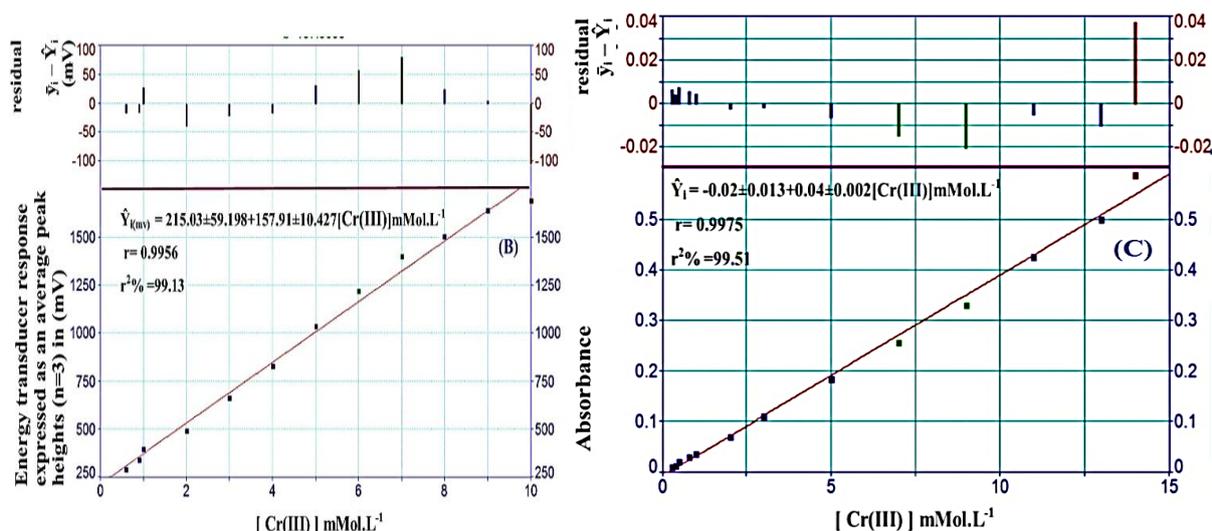


Fig. 8: Calibration graph for the variation of [Cr(III) ] on:

- (A): Response profile verses time
- (B): Transducer energy response expressed by linear equation using Ayah 6SX1-ST-2D Solar-CFIAnalyser , residual ( $\bar{y}_i - \hat{Y}_i$ ),  $\bar{y}_i$ : practical value,  $\hat{Y}_i$ : estimate value.
- (C):Calibration graph using UV-Vis SP for determination of[Cr(III)] , for measurement of Abs , Residual ( $\bar{y}_i - \hat{Y}_i$ ),  $\bar{y}_i$ : practical value,  $\hat{Y}_i$ : estimate value.

Table 7: Summary of calibration graph for Cr(III) ion– MFA system

Type of method	Measured[X]mMol.L <sup>-1</sup>	n	Range of [X] mMol.L <sup>-1</sup>	$\hat{Y}_{i(mv)} = a \pm s_a t + b \pm s_b t [X] \text{mMol.L}^{-1}$ At confidence interval 95%, n-2	r r <sup>2</sup> r <sup>2</sup> %	t <sub>tab</sub> at 95 % , n-2	Calculate d t-value $\frac{ r /\sqrt{n-2}}{\sqrt{1-r^2}}$	L.O.D from gradual dilution
				$\hat{Y}_i = a \pm s_a t + b \pm s_b t [X] \text{mMol.L}^{-1}$ At confidence level 95%, n-2				
Ayah 6SX1-ST-2D solar cell CFIA	0.4-11	12	0.6-10	$215.03 \pm 59.198 + 157.91 \pm 10.427 [\text{Cr(III)}] \text{mMol.L}^{-1}$	0.9956 0.9913 99.13%	2.228 << 33.72		400 μMol.L <sup>-1</sup>
UV-Vis SP.	0.3-14	13	0.3-14	$-0.02 \pm 0.013 + 0.04 \pm 0.002 [\text{Cr(III)}] \text{mMol.L}^{-1}$	0.9975 0.9951 99.51 %	2.201 << 47.26		100 μMol.L <sup>-1</sup>

$\hat{Y}_i$ =estimate value, r = correlation coefficient, r<sup>2</sup>= coefficient of determination (C.O.D), r<sup>2</sup>% = Linearity percentage, n: no. of measurement , [X]: conc. of [Cr(III)] .

**Limit of detection (L. O. D)**

A study was carried out to determine the limit of detection of Cr(III)ion by three different methods : gradual dilution of minimum concentration in the linear range , theoretical based on the value of slope and from the linear regression plot. **Table 8** tabulated all these calculation value of detection limit for 145 μL sample volume.

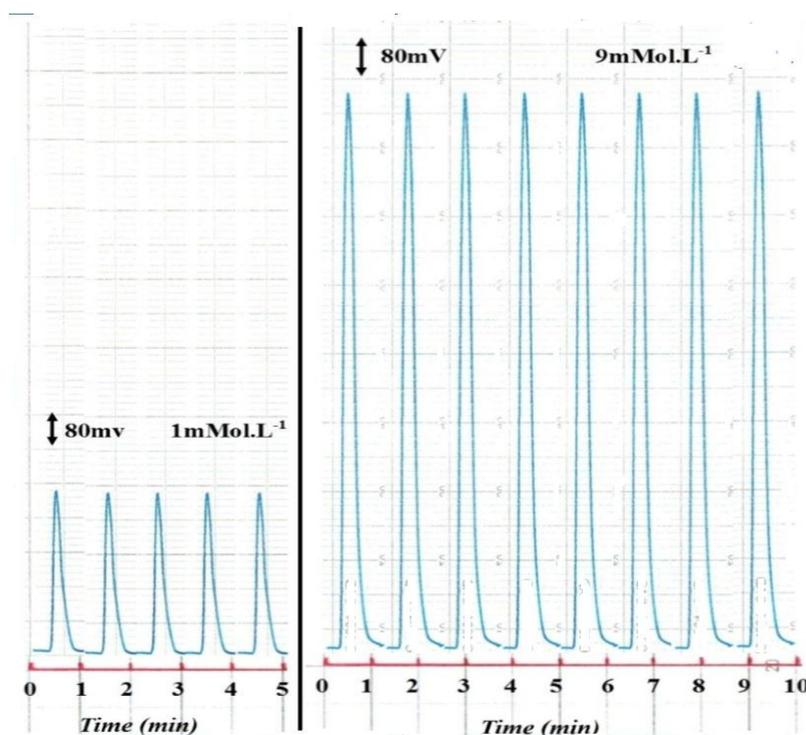
Table 8: Summary of limit of detection based on different approaches

Practically based on the gradual dilution for the minimum concentration	Theoretical based on the value of slope $x = 3S_B/\text{slope}$ for n=13	Theoretical based on the linear equation $\hat{Y} = Y_B + 3S_B$
(0.4 mMol.L <sup>-1</sup> ) 15.46 μg/sample	73.41 ng/sample	37.68 μg/sample

X= value of L.O.D based on slope, S<sub>B</sub>=standard deviation of blank repeated for 13 times, Y<sub>B</sub>=Average response for blank= intercept, L.O.D=limit of detection,  $\hat{Y}$ = estimated value

### Repeatability

The repeatability of measurement and the efficiency of homemade Ayah 6SX1-ST – 2D solar cell CFIA Analyser were studied at  $(1,9) \text{ mMol.L}^{-1}$  of Cr(III) ion were used, using the optimum parameters. The repeated measurements for five and eight successive injections were measured. The percentage of relative standard deviation less than 0.2 %, indicate a reliable measurement can be achieved using this method. **Figure 9** shows response profile of repeatability. The obtained results were summarized in **Table 9**.



**Fig. 9: Profile of successive repeatability measurements of Cr(III) ion using Ayah 6SX1-ST – 2D solar cell CFIA Analyser**

**Table 9: Repeatability of Cr(III) ion results obtained for the formation of precipitate colored species**

Conc. $\text{mMol.L}^{-1}$	Conc.	Average response $\bar{y}_i(\text{mV})$	RSD %	$\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$ At confidence interval 95%	Number Of injection
1		441	0.08	$441 \pm 0.438$	5
9		1640	0.11	$1640 \pm 1.508$	8

$$t_{0.025, 4} = 2.776, \quad t_{0.025, 7} = 2.365$$

### Evaluation of the use of Ayah 6SX1-ST-2D- Solar cell CFI Analyser for the determination of Cr(III) in pure formulation as an application

The adopted method was used for the determination of chromium (III) ion in pure formulation (Chromium (III) nitrate nonahydrate, Sigma aldrich-Germany). Using homemade Ayah 6SX1-ST-2D-Solar cell CFI Analyser supplier with six snow whitelight emitting diodes (LEDs) as a source for measuring turbidity via reflecting of incident light in addition to the classical method. A series of solutions were prepared of pure formulation (Chromium (III) nitrate nonahydrate)  $0.1 \text{ Mol.L}^{-1}$  by transferring 0.25 mL to each of the five volumetric flask (25 mL), followed by the addition of gradual volumes of  $0.1 \text{ Mol.L}^{-1}$  standard chromium (III) ion (0, 0.25, 0.5, 0.75, 1) ml which equivalent to (0, 1, 2, 3, 4)  $\text{mMol.L}^{-1}$  in the case of use Ayah 6SX1-ST-2D Solar cell –CFI Analyzer, while transferring 0.2 ml from  $0.1 \text{ Mol.L}^{-1}$  pure formulation to each of the five volumetric flask (25 ml), followed by the addition of gradual volumes of  $0.1 \text{ Mol.L}^{-1}$  standard chromium (III) ion (0, 0.2, 0.25, 0.5, 0.75) ml in order to have (0, 0.8, 1, 2, 3)  $\text{mMol.L}^{-1}$  in the case of use classical UV-Vis spectrophotometric method. Flask no.1 is the sample. **Figure 10 A** shows the responses profile for this study. **Figure 10 B**

represented standard addition calibration graphs using Ayah 6SX1-ST-2D solar cell –CFI Analyser. The paired t-test in two methods represented as :

◆ Individual paired t-test

- Development method (Ayah 6SX1-ST-2D solar cell –CFI Analyser) ,

There is no significant difference between the means for (Chromium (III) ion ,Sigma aldirch-Germany) and theoretical value ( $\mu_0=100 \text{ mMol.L}^{-1}$ ) , (i.e:  $H_0$  is accepted )

- Classical method (UV-Vis Spectrophotometric)

There is a significant difference between the means for (Chromium (III) ion ,Sigma aldirch-Germany) and theoretical value ( $\mu_0=100 \text{ mMol.L}^{-1}$ ) , (i.e:  $H_1$  is accepted ) due to the interferences effect . **Table 10** sum up all results for two methods .

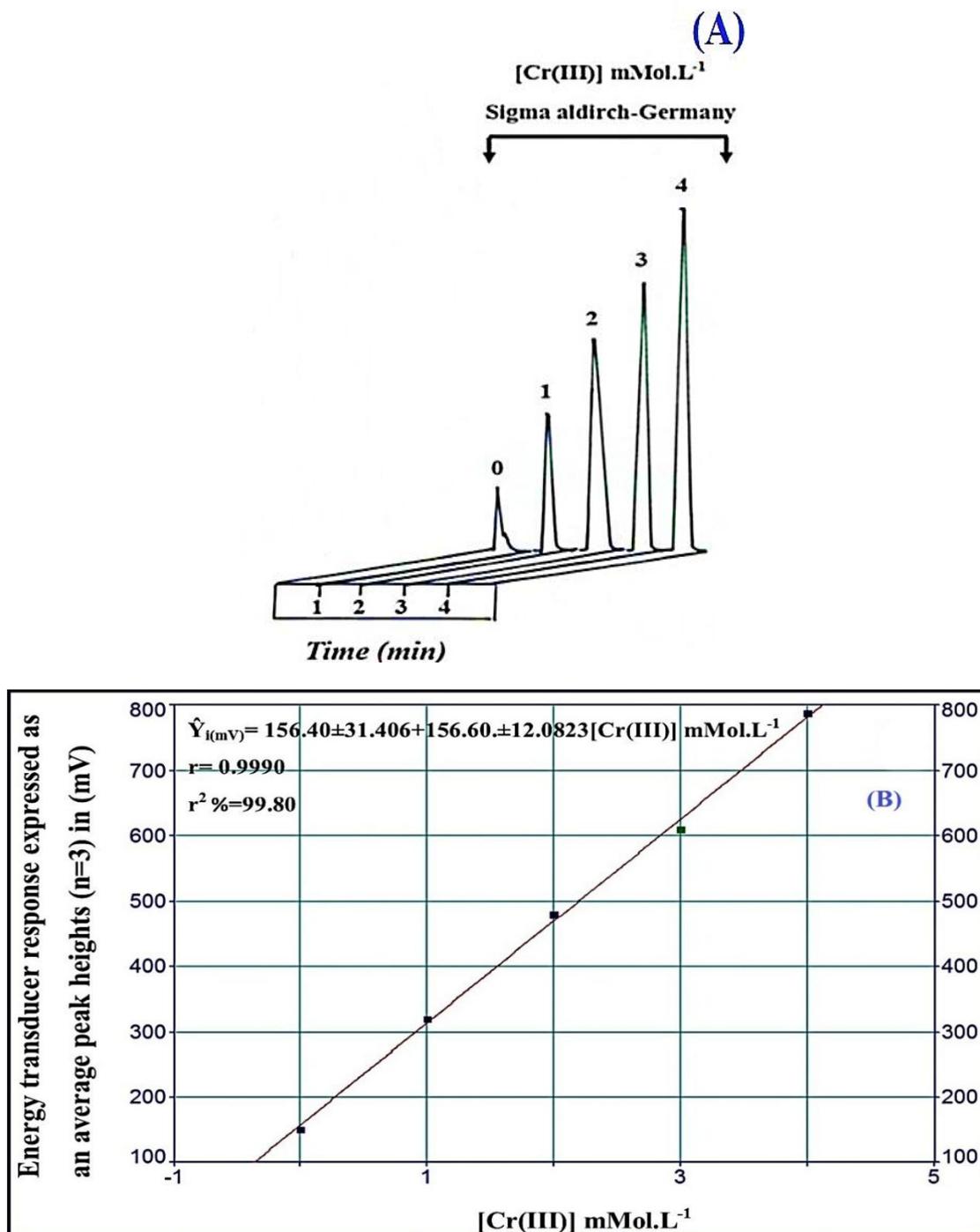


Fig. 10: Standard addition calibration graph for different samples using Ayah 6SX1-ST-2D solar cell - CFI Analyser.

(A): Response profile versus time .

(B): Chromium (III) nitrate nonahydrate, Sigmaaldirch, Germany

**Table 10: Results for the determination of chromium (III) ion in pure formulation using standard addition, with two methods Ayah 6SX1-2D solar cell CFIA and UV-Vis spectrophotometric method**

Analyte	Sample commercial name, company country.	Theoretical Weight of chromium(III) ion in 100 mL (g)	Theoretical concentration in 100 mL	Equation of standard addition curve at 95% for n-2		$r$ $r^2$ %	Practical concentration in 25 mL	Practical concentration in 100 mL	Practical weight in 100 ml (g)	Efficiency of determination (Rec %)	Individual comparison ( $\bar{w}_i - \mu_0$ )/ $\sqrt{n}\sigma_n$ 1 Ayah 6SX1-ST-2 D Solar cell-CFI Analyser with Quoted value $t_{0.05/2, 2}=4.303$	$E_{err}$ %						
				$\hat{Y}_{i(mv)}=a\pm s_a t+b\pm s_b t[Cr(III)]mMol.L^{-1}$	$\hat{Y}_i^*=a\pm s_a t+b\pm s_b t[Cr(III)]mMol.L^{-1}$								Ayah 6SX1-ST-2D Solar cell					
				UV - Vis spectrophotometer														
Cr(III)	Chromium (III)nitrate nonahydrate, Sigma aldirch, Germany	0.5199	100	$156.40\pm 31.406+156.60\pm 12.823[Cr(III)]mMol.L^{-1}$	0.9990 0.9980 99.80%	0.999 9	99.872±4.546	0.519	99.87%	$ -0.121  \ll 4.303$	$ -0.13 $							
				$0.0323\pm 0.006+0.0331\pm 0.003[Cr(III)]mMol.L^{-1}$	0.9988 0.9976 99.76%	0.976 6	121.979±4.919	0.634	121.98%	$19.227 \gg 4.303$	21.98							

$\hat{Y}_i$  = estimated value .

## CONCLUSION

The suggested methods is simple, sensitivities and rapid. Application of the proposed methods to the analysis of Cr (III) ion in pure formulation based on formation yellowish greencolor precipitate as an ion- pair compound for the reaction of Cr (III) ion with mefenamic acid in aqueous medium . It was shown that with no doubt that newly developed method is a good as the classical method. An alternative analytical method is found through this research work, which based on simple parameter conditions.

## REFERENCES

1. Tom C and Narayana B. Spectrophotometric determination of chromium using saccharin. *Indian Journal of Chemical Technology*. 2005;12:596-600 .
2. Fawcett and Eric . Spin-density-wave anti ferromagnetism in chromium. *Reviews of Modern Physics*. 1998;60:209-283.
3. Wang CF, Chin CJ, Luo SK and Men LC. Determination of chromium In airborne particulate matter by high resolution and laser ablation inductively coupled plasma mass spectrometry. *Anal ChimActa* . 1999;389:257 -266.
4. Gurley H and Wallschlaeger D. Determination of chromium(III) and chromium(VI) using suppressed ion chromatography inductively coupled plasma mass spectrometry. *J Anal Atom Spectrum*. 2001;16:926-932.
5. Makishima A, Kobayashi K and Nakamura E. Determination of Chromium, Nickel, Copper and Zinc in Milligram Samples of Geological Materials, *Geostandards newsletter*. 2002; 26(1):41-51.
6. Eng TY, Jiang ZC, Hu B and Liao ZH. Catalytic Spectrophotometric Determination of Chromium. *Fresen J Anal Chem*. 1999;364:551-555.
7. Imran A and Hassan YA. Speciation of arsenic and chromium metal ions by Reversed phase high performance liquid chromatography. *Chemosphere*. 2002;48:275-278.
8. Balasubramanian S and Pugalenti V. Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV-vis spectrophotometric methods. *Talanta*. 1999;50(3):457-467.
9. Monteiro MI, Fraga IC, Yallouz AV, Oliveira NM and Ribeiro SH. Determination of total chromium traces in tannery effluents by electrothermal atomic absorption spectrometry,

- flame atomic absorption spectrometry and UV–vis spectrophotometric methods. *Talanta*. 2002;58(4):629-633.
10. Jeffery G, Bassett J, Menghan J and Denney R. *Quantitative Chemical analysis*, Fifth Edition, New York. 1909;779-813.
  11. Peter JW and Bruce AM. *Atomic absorption data book*, Fourth Edition, PyeunicamLtd .Cambridge (England). 1981.
  12. Miler JC and Miler JN. *Statistics for analytical chemistry*. 2nd ed. John Wiley and N.Y.Sons. 1988.
  13. Bluman AG. *Elementary statistics*. 3<sup>rd</sup> edition . WCB/ MC Graw– Hill, New York, 1997.