

CONTINUOUS FLOW INJECTION TURBIDIMETRIC FOR DETERMINATION OF ZINC (II) ION BY ION PAIR COMPLEX WITH MEFENAMIC ACID USING AYAH 6SX1-ST-2D SOLAR CELL CFI ANALYSER

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ABSTRACT

A new turbidimetric method characterized by simplicity, accuracy and speed for determination of zinc (II) ion in pure and pharmaceutical preparation by continuous flow injection analysis. The method was based on the formation of ion pair compound between zinc (II) ion and mefenamic acid (MFA) in an aqueous medium for the formation of yellow precipitate and this precipitate was determined using homemade Linear Array Ayah6SX1-ST-2D Solar cell continuous flow injection analyser. The optimum parameters, concentrations of chemical reactants and physical instrumental conditions have been investigated. Data treatment shows that linear range 5-16 mMol.L⁻¹ while L.O.D was 79.05 µg/sample from the stepwise dilution of minimum concentration for the lowest concentration in the linear dynamic range of the calibration graph. The correlation coefficient (r) was 0.9977 while percentage linearity (%r²) C.O.D was 99.55%. R.S.D% for the repeatability (n=5,8) < 0.2% for concentration 8 and 15 mMol.L⁻¹ respectively of zinc (II) ion. The method was applied successfully for the determination of zinc (II) ion in pharmaceutical drugs. A comparison was made between the developed method with the classical method via the use of paired t-test. It shows that there were a significant differences between two methods at 95 % confidence level and no significant difference between two drugs.

Keywords: Zinc(II) ion, Flow injection analysis, Turbidity.

INTRODUCTION

Zinc is a chemical element with symbol Zn and atomic number 30. It is the first element of group 12 of the periodic table. In some respects zinc is chemically similar to magnesium: its ion is of similar size and its only common oxidation state is +2. Zinc is the 24th most abundant element in Earth's crust and has five stable isotopes. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral. The largest mineable amounts are found in Australia, Asia, and the United States¹. Zinc production includes froth flotation of the ore, roasting, and final extraction using electricity (electrowinning). Zinc is available as bluish-white appearances, solid phase, 419.53 °C melting point, 7.14 g/cm³ density and electron configuration is [Ar] 3d¹⁰ 4s^{2,3}. A number of analytical methods have been developed for the quantitative determination of zinc (II) ion in dosage forms and pharmaceutical samples. Among those are spectrophotometry⁴⁻⁷, polarography⁸.

This paper describes a simple and rapid turbidimetric flow injection method for determination of zinc (II) ion in pharmaceutical preparation. The method uses mefenamic acid as a precipitating reagent in aqueous medium. Yellow precipitate is formed as ion pair complex. The precipitate is measured by the reflection of incident light using Ayah 6SX1-ST-2D Solar cell CFI Analyser.

EXPERIMENTAL

REAGENTS AND CHEMICALS

A standard solution (0.1 Mol.L^{-1}) of Zn (II) ion was prepared by dissolving 1.3629 g of zinc chloride (ZnCl_2 , $136.29 \text{ g.mol}^{-1}$, BDH) in 100 ml of distilled water. A stock solution (0.1 Mol.L^{-1}) of mefenamic acid ($\text{C}_{15}\text{H}_{15}\text{NO}_2$, 241 g.mol^{-1} , SDI) was prepared by dissolving 2.41 g in 100 mL of 0.1 Mol.L^{-1} NaOH. 0.1 Mol.L^{-1} of Sodium hydroxide solution (NaOH, 40 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 Mol.L^{-1} sodium carbonate (Na_2CO_3 , $105.99 \text{ g.mol}^{-1}$, BDH)).

All chemicals used were of analytical-reagent grade and distilled water used to prepare the solutions.

Sample Preparation

Forty tablets weight, crushed and grinded. The drug supplier (Zinc Sulphate, 125mg, Natra Health and Zinc Sulphate, 220 mg, Geri Care) containing 45 mg, 50 mg respectively of Zinc (II) ion were weight i.e. 8.6225, 5.6226 g respectively which is equivalent to 0.6541g of active ingredient (0.1 Mol.L^{-1}) concentration of Zinc (II) ion for each drug. The powder was dissolved in distilled water followed by filtration to remove any undissolved residue affecting on the response and complete the volume to 100 mL with the same solvent.

Apparatus

Peristaltic pump – 2 channels variables 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 spectrophotometer digital double beam type UV-1800, Shimadzu, Japan was used to scan the spectrum of Zinc (II) ion using 1 cm quartz cell. Figure 1 shows The flow system used for the determination of Zinc (II) ion.

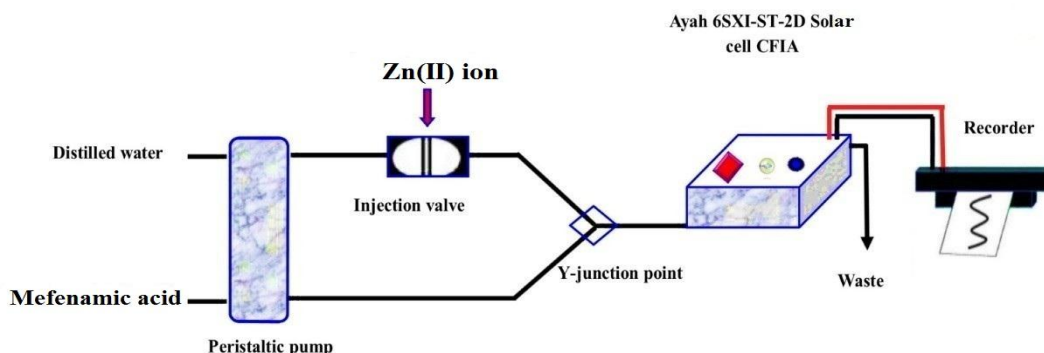
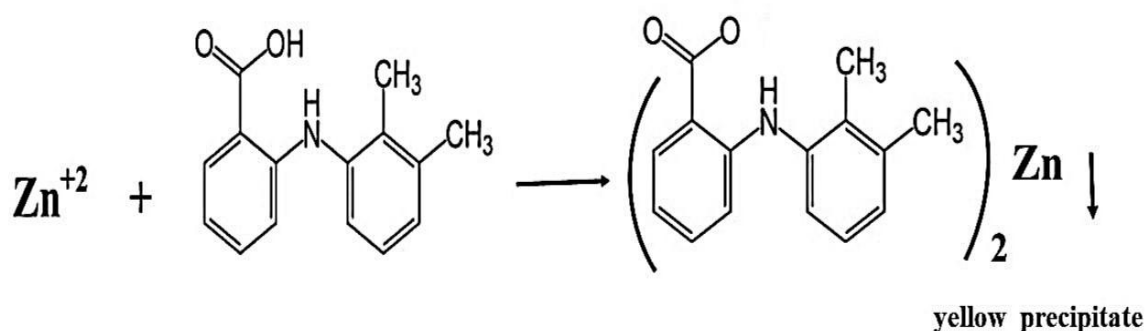


Fig. 1: Flow diagram manifold system used for the determination of Zinc (II) ion

Methodology

The manifold system for the determination of Zinc (II) ion via precipitation reaction with mefenamic acid to form a yellow color precipitate as an ion pair is composed of two lines as shown in figure 1. The first line represents the carrier stream (Distilled water) at 1.7 mL.min^{-1} flow rate which leads to the injection valve to carry Zinc (II) ion, sample volume $145 \mu\text{L}$; while the second line supplies mefenamic acid (3 mMol.L^{-1}) solution at 2.1 mL.min^{-1} . Both lines mix together at a Y-junction made from methyl methacrylate polymer. The reflection of incident light peak of the resulting yellow precipitate is followed using Linear Array Ayah 6SX1-ST-2D-CFI analyser and the variation of response was monitored using six snow-white light emitting diodes (LEDs). Each solution was assayed in triplicate. 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 Zinc (II) ion - mefenamic acid system is represented in scheme 1.



Scheme. 1: Proposed mechanism of reaction between Zinc (II) ion and mefenamic acid

RESULT AND DISCUSSION

Study of optimum parameters

The chemical parameters as well as physical parameters were investigated. These variables were optimized by making all variables constant and varying one each at time.

Chemical Variables

Mefenamic acid Concentration

15 mMol.L⁻¹ of Zn(II) ion was injected through the carrier stream (distilled water) with 122 μL sample volume at a flow rate 1.3, 1.7 mL.min⁻¹ for carrier stream and reagent respectively. Using different concentration of mefenamic acid (0.7-6) mMol.L⁻¹ and 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⁻¹, while at higher concentration (> 3 mMol.L⁻¹) lead to decrease of response height. It really might be attributed to increase of the density of the precipitate colored product which prevents the light of LEDs to arrival to the detector (twin solar cell). Therefore 3 mMol.L⁻¹ of mefenamic acid was regarded as the optimum concentration for the determination of Zn(II) ion, that used for the further work. The results were summarized in **Table 1**.

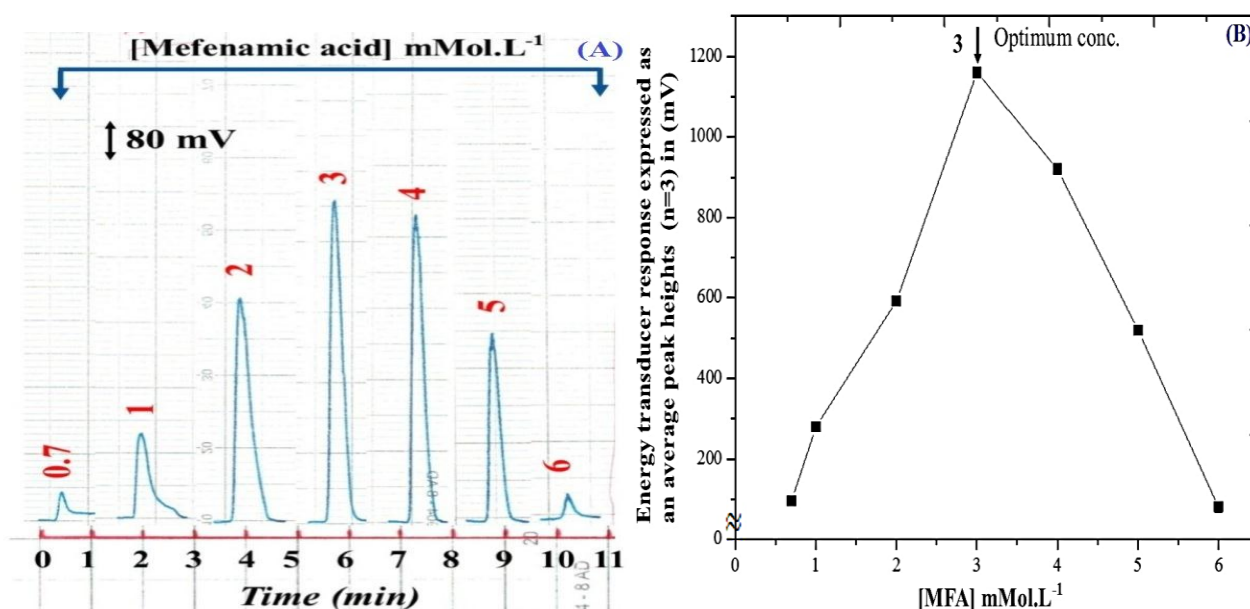


Figure 2: Effect of [MFA] on:
(A): Profile versus time using different concentration of MFA.
(B): Energy transducer response in mV for Zn(II) ion-MFA system.

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

[MFA] mMol.L ⁻¹	Energy transducer response expressed as an average peak heights (n=3) \bar{y}_i in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$
0.7	96	0.13	96 ± 0.310
1	280	0.05	280 ± 0.348
2	592	0.04	592 ± 0.588
3	1160	0.03	1160 ± 0.865
4	920	0.04	920 ± 0.914
5	520	0.05	520 ± 0.646
6	80	0.26	80 ± 0.517

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

Using 15 mMol.L⁻¹ of Zn(II)ion, The effect of NaOH on the precipitation of Zn(II)ion was studied. 3 mMol.L⁻¹ of mefenamic acid was used as the precipitate agent, achieved in previous section. Variable concentrations of NaOH (0.5-10 mMol.L⁻¹) were prepared as a carrier stream for the Zn(II)ion, in addition to the use of distilled water as a carrier stream, 122 μ L of sample volume at 1.3, 1.7 mL.min⁻¹ flow rate of carrier stream and reagent respectively. **Figure 3 A,B** shows the decrease of peak height with increase of NaOH concentration. It might be attributed that an increase the basic concentration of the medium leads to precipitation of Zn(II)ion as a hydroxides previous to precipitate with mefenamic acid. Therefore, the neutral medium (distilled water) was selected as the optimum medium for (Zn(II) ion – MFA system). The obtained results are tabulated in **Table 2**.

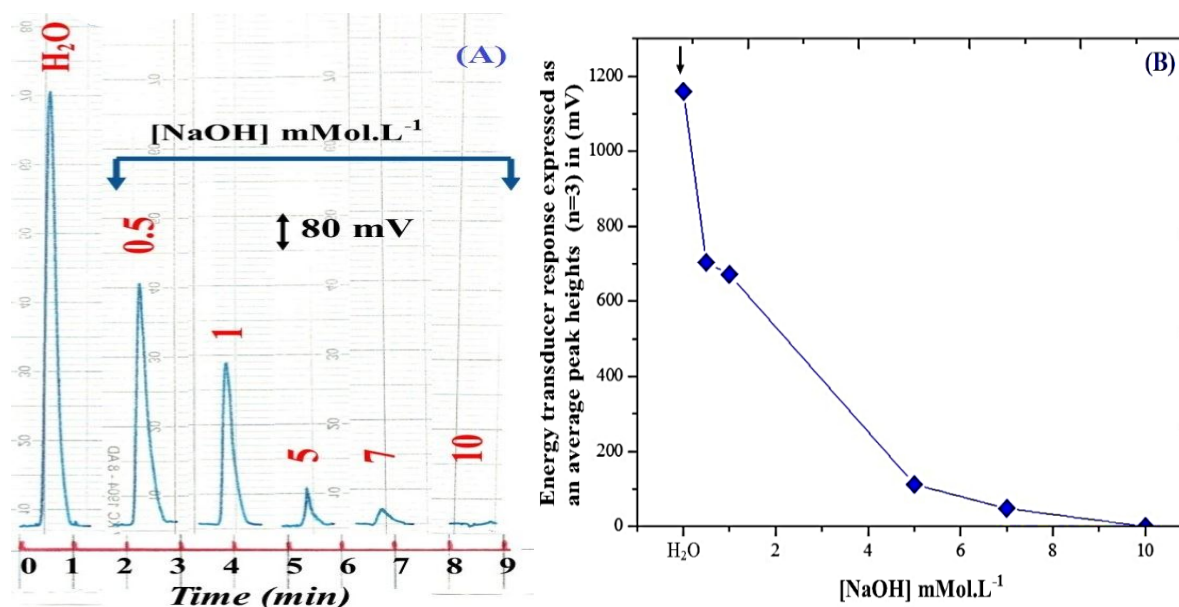


Fig. 3: Variation of concentration of basic medium as a carrier stream on:
(A): Response profile using Ayah 6SX1-ST-2D solar cell CFIA, for determination of Zn(II)ion
(B): Transducer energy response (mV)

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

[NaOH] mMol.L ⁻¹	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 ₂ O	1160	0.03	1160 ± 0.865
0.5	704	0.04	704 ± 0.700
1	672	0.03	672 ± 0.501
5	112	0.19	112 ± 0.529
7	48	0.40	48 ± 0.477
10	0	0	0 ± 0

Physical Variables

Flow rate

3 mMol.L⁻¹ of MFA with 15 mMol.L⁻¹ of Zn(II)ion were used, a set of experiments were conducted for the optimization of the preferred flow rate 0.3-2.6 mL.min⁻¹ for carrier stream (distilled water) and 0.4-3.4 mL.min⁻¹ for reagent (mefenamic acid). 1.9 V, applied voltage to the light emitting diodes (LEDs) with 122 μL injected volume for Zn(II) 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 4 A,B), (i.e. 0.3 mL.min⁻¹) and increase in peak base width (Δt_B), while at higher flow rate (i.e. >0.9, 1.3 mL.min⁻¹) for carrier stream and reagent respectively there was an increase in peak height up to 1.7 & 2.1 mL.min⁻¹ followed by decrease in response; 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 Zn(II)ion –MFA system was 1.7 and 2.1 mL.min⁻¹ 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.

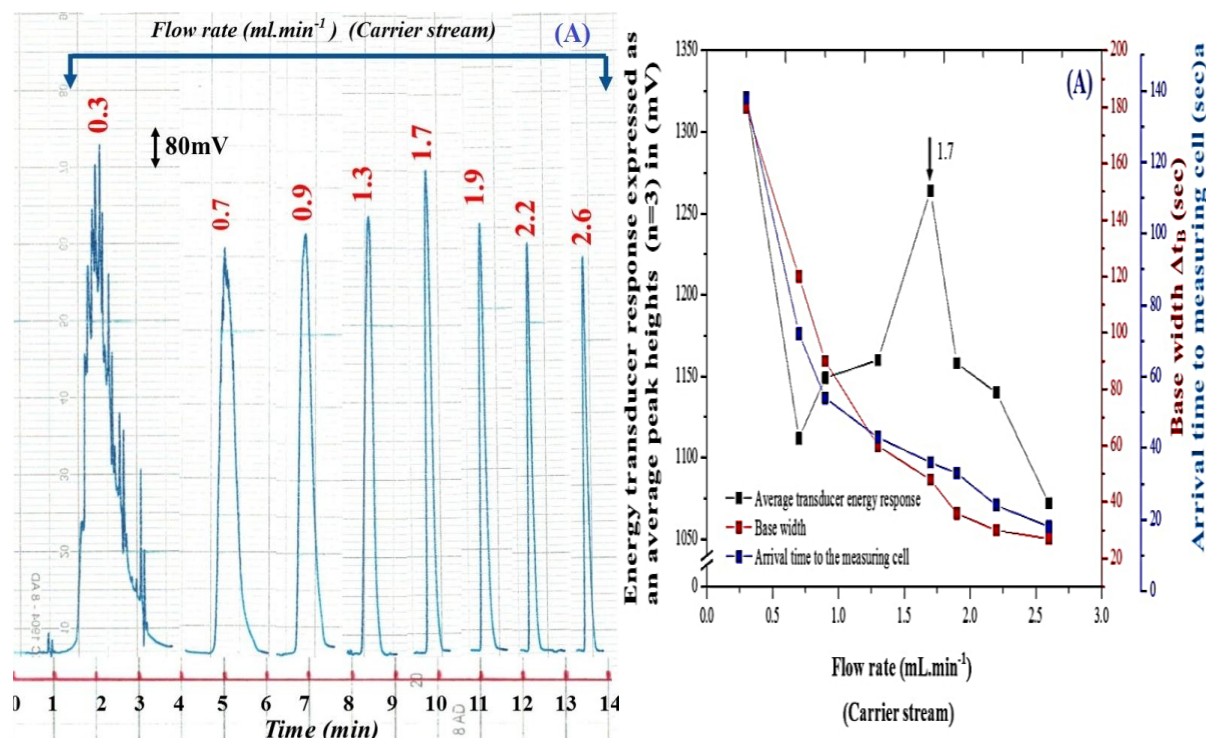


Fig. 4: Effect of the variation of flow rate on:

(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 Zn(II) ion (15 mMol.L⁻¹)-[MFA]system using 122 μ L sample volume

Peristaltic Pump speed	flow rate mL.min ⁻¹		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 Δt_B (sec)	t^* (sec)	V* (mL)	C* (mMol.L ⁻¹)
	Line 1	Line 2							
5	0.3	0.4	1320	0.01	1320 \pm 0.328	180	138	2.222	0.824
10	0.7	0.8	1112	0.02	1112 \pm 0.553	120	72	3.122	0.586
15	0.9	1.3	1149	0.03	1149 \pm 0.856	90	54	3.422	0.535
20	1.3	1.7	1160	0.03	1160 \pm 0.865	60	43	3.122	0.586
25	1.7	2.1	1264	0.03	1264 \pm 0.942	48	36	3.162	0.579
30	1.9	2.6	1158	0.04	1158 \pm 1.151	36	33	2.822	0.648
35	2.2	2.8	1140	0.04	1140 \pm 1.133	30	24	2.622	0.698
40	2.6	3.4	1072	0.04	1072 \pm 1.065	27	18	2.822	0.648

Δt_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 Zn(II)ion (15 mMol.L⁻¹)–MFA (3 mMol.L⁻¹) system , 1.7 and 2.1 mL.min⁻¹ 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 μ L 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 (Δt_B) of response is increase (i.e. increase analysis time) with increase sample volume .Therefore: 145 μ L was chosen as the optimum sample volume for Zn(II)ion to obtain regular response , sharp maxima peak and less consumption of chemical solutions .**Table 4** summarized the results obtained.

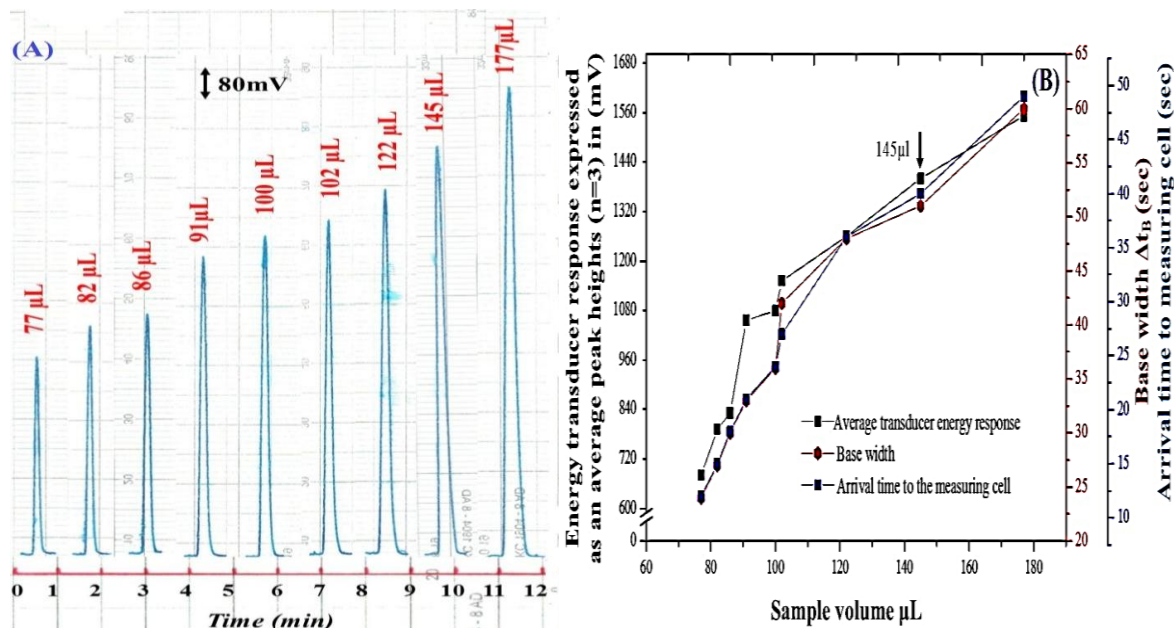


Fig. 5: Effect of the variation of sample volume on:

(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 Zn(II)ion using Ayah 6XS1-ST-2D Solar cell CFIA

Sample volume μL	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 Δt_B (sec)	t^* (sec)
77	680	0.04	680 ± 0.676	24	12
82	792	0.03	792 ± 0.590	27	15
86	832	0.04	832 ± 0.827	30	18
91	1056	0.04	1056 ± 1.049	33	21
100	1080	0.06	1080 ± 1.610	36	24
102	1152	0.06	1152 ± 1.717	42	27
122	1260	0.05	1260 ± 1.565	48	36
145	1400	0.05	1400 ± 1.739	51	40
177	1552	0.05	1552 ± 1.928	60	49

Δt_B : Base width of response

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

Effect of Purge Time

The optimum parameters that achieved in previous sections (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) for Zn(II)ion($15\text{mMol}\cdot\text{L}^{-1}$)–MFA ($3\text{mMol}\cdot\text{L}^{-1}$) system were used . A study was carried out to determine the optimum allowed permissible time for the sample segment to be injected from the injection valve. Variable times (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 35 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 ; 35sec 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**.

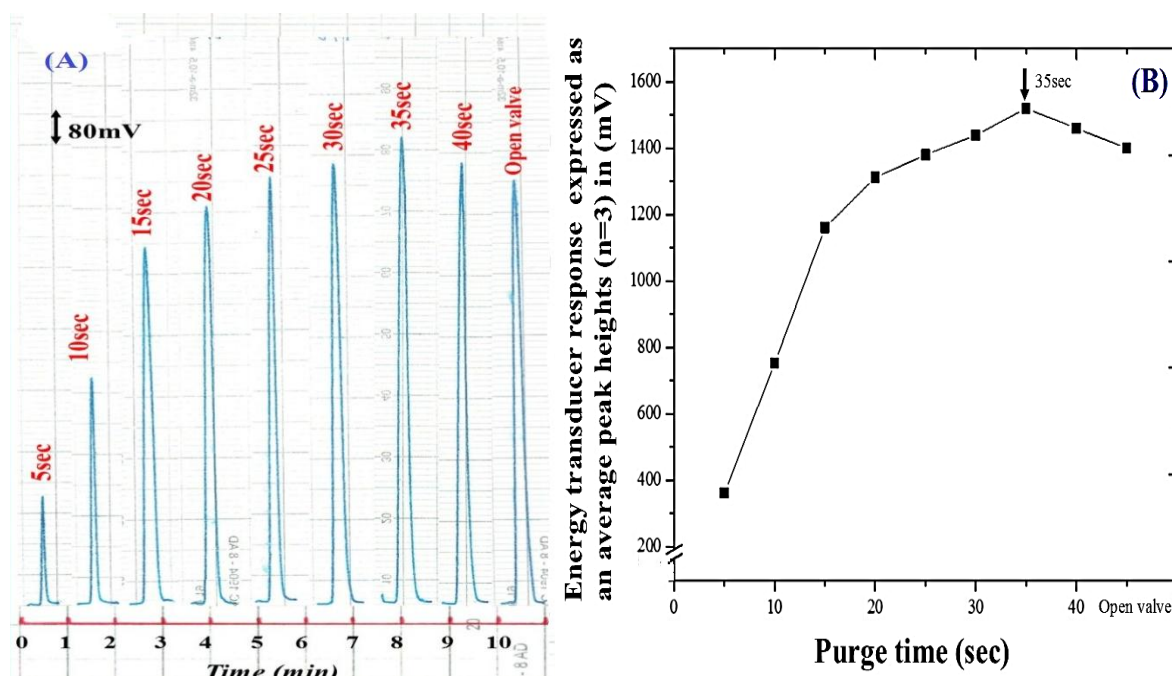


Fig 6: Effect of the variation of purge time on:
(A): Response profile (i.e: via reflection of incident light by precipitate species) versus time.
(B): Energy transducer response in (mV) using Zn(II)ion $15\text{mMol}\cdot\text{L}^{-1}$ –MFA - $3\text{mMol}\cdot\text{L}^{-1}$ system

Table 5: Effect of the variation of purge time on the energy transducer response for the determination of Zn(II) ion using 145 μ L

Pu 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	360	0.04	360 \pm 0.358
10	752	0.06	752 \pm 1.121
15	1160	0.03	1160 \pm 0.865
20	1312	0.05	1312 \pm 1.630
25	1380	0.11	1380 \pm 3.771
30	1440	0.17	1440 \pm 6.082
35	1520	0.23	1520 \pm 8.685
40	1460	0.22	1460 \pm 7.980
Open valve	1400	0.37	1400 \pm 12.869

Incident light intensity

Ayah 6SX1- ST-2D solar cell CFIA is characterized by the capability of variation of incident light . Variable intensity of light source was used 0.16 – 2.1 volt 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 were used ; 1.7 mL.min⁻¹ flow rate for carrier stream (distilled water) and 2.1mL.min⁻¹ for reagent line , 145 μ L sample volume , and 35 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 $r = 0.9881$. 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**.

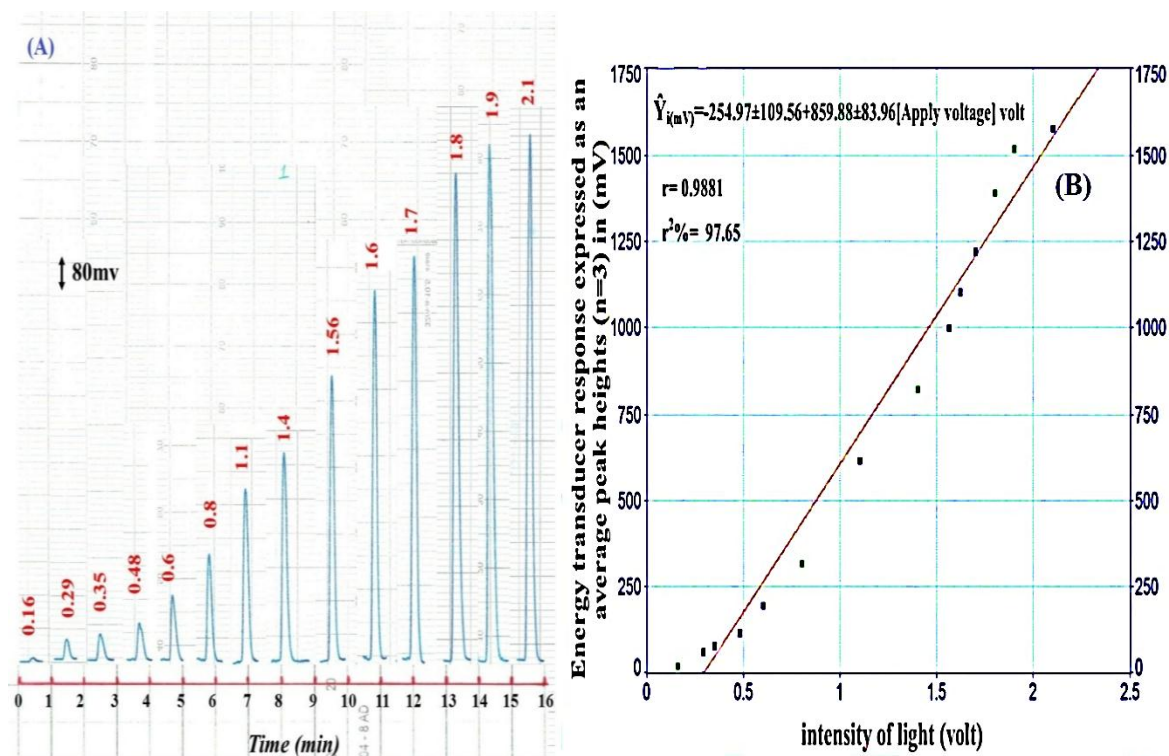


Fig. 7: Variation of incident light intensity on:
(A): Response profile for Zn(II)ion-MFA system.
(B): Calibration graph for the variation of applied voltages on the energy transducer response using linear equation

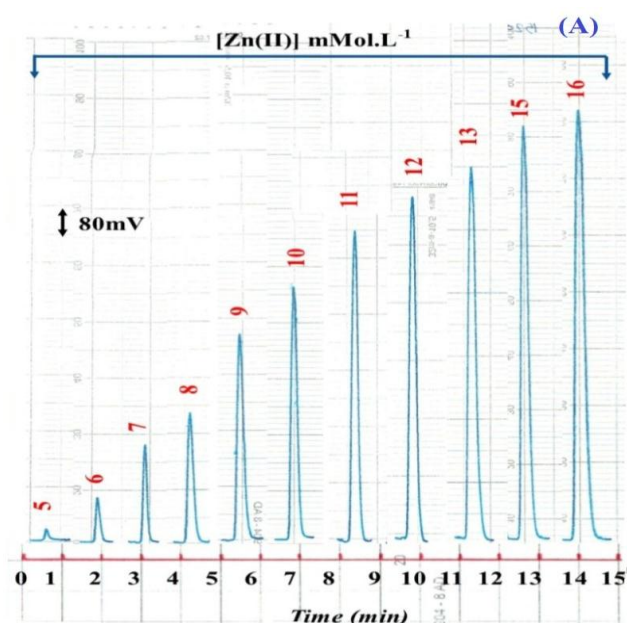
Table 6: Variation of incident light intensity on transducer energy response

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%) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$
0.16	24	0.23	24±0.137
0.29	64	0.26	64±0.413
0.35	80	0.29	80±0.576
0.48	120	0.37	120±1.103
0.6	200	0.42	200±2.087
0.8	320	0.44	320±3.498
1.1	616	0.37	616±5.662
1.4	824	0.51	824±10.440
1.56	1000	0.56	1000±13.912
1.6	1104	0.44	1104±12.068
1.7	1224	0.21	1224±6.386
1.8	1392	0.08	1392±2.767
1.9	1520	0.06	1520±2.266
2.1	1580	0.03	1580±1.178

Calibration graph

A series of solutions of Zn(II) ion (3-16) mMol.L⁻¹ were prepared in order to prepare a scatter plot diagram as shown in **Figure 8 A**, using the optimum parameters achieved in previous section . 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 Zn(II)ion . A straight line graph ranging from (5 – 16) mMol.L⁻¹ with correlation coefficient (r):0.9977 as shown in **Figure 8 B** . Above 16 mMol.L⁻¹for Zn(II)ion, It was noticed, a broad in the peak height was observed and increase of the base width (Δt_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.

While the UV- Spectrophotometric (classical method) at $\lambda_{max}= 213.9$ nm [9,10],the calibration graph was established to determination of Zinc (II) ion from (0.6-18) mMol.L⁻¹ with correlation coefficient (r): 0.9993 (**Figure 8 C**) with 300 μ Mol.L⁻¹ detection limit . The results obtained were tabulated in **Table 7** , including the summary of linear regression for the variation of energy transducer response with [Zn(II)] using first degree equation of the form $\hat{y}=a\pm s_a t+b\pm s_b t$ [11,12] 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.



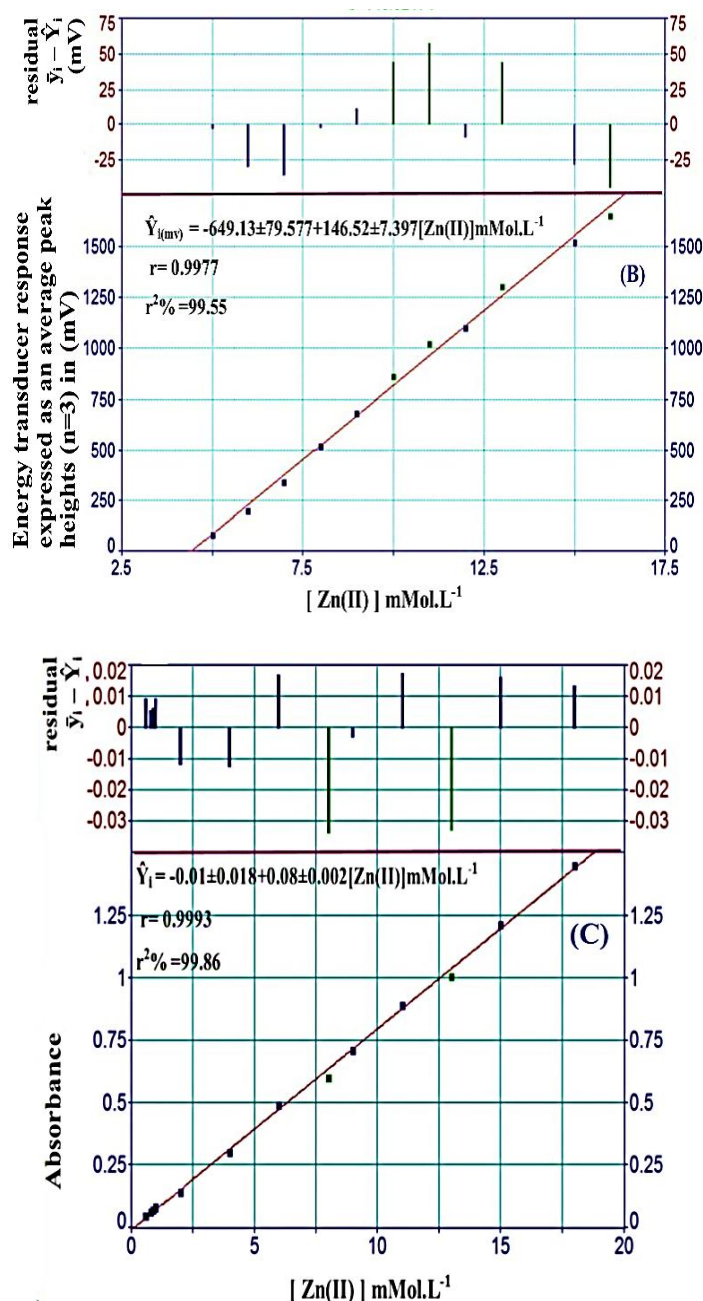


Figure 8: Calibration graph for the variation of [Zn(II)] on:

- (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-SP. for determination of [Zn(II)] , 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 Zn(II)ion– MFA system

Type of method	Measured [X] mMol.L ⁻¹	n	Range of [X] mMol.L ⁻¹	$\hat{Y}_{i(mv)} = a \pm s_a t + b \pm s_b t [X] \text{mMol.L}^{-1}$ At confidence interval 95%, n-2	r r ² r ² %	t _{tab} 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 CFI	3-16	11	5-16	$-649.13 \pm 79.577 + 146.52 \pm 7.397 [\text{Zn(II)}] \text{mMol.L}^{-1}$	0.9977 0.9955 99.55%	2.262	<< 44.76	4 mMol.L ⁻¹
UV-SP.	0.6-18	13	0.6-18	$-0.01 \pm 0.018 + 0.08 \pm 0.002 [\text{Zn(II)}] \text{mMol.L}^{-1}$	0.9993 0.9986 99.86%	2.201	<< 89.25	300 μMol.L ⁻¹

\hat{Y}_i =estimate value, r = correlation coefficient, r²= coefficient of determination (C.O.D), r²% = Linearity percentage, n: no. of measurement, [X]: conc. of [Zn(II)].

Limit of detection (L. O. D)

A study was carried out to determine the limit of detection of Zn(II)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 $\hat{Y} = Y_B + 3S_B$
(4 mMol.L ⁻¹) 79.05 μg/sample	60.69 ng/sample	15.08 μg/sample

X= value of L.O.D based on slope, S_B=standard deviation of blank repeated for 13 times, Y_B=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 CFI Analyser were studied at (8,15) mMol.L⁻¹ of Zn(II)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**.

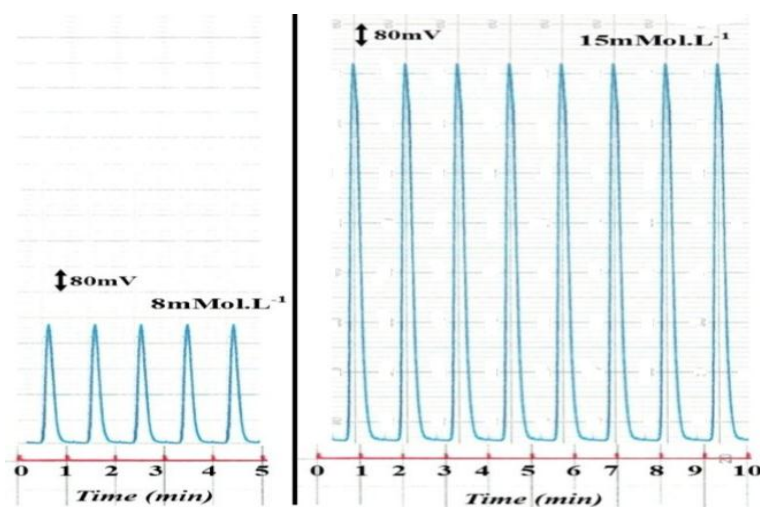


Figure 9: Profile of successive repeatability measurements of Zn(II)ion using Ayah 6SX1-ST –2D solar cell CFI Analyser

Table 9: Repeatability of Zn(II)ionresults obtained for the formation of precipitate colored species

Conc. mMol.L ⁻¹	Average response \bar{y}_i (mV)	RSD %	$\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$ At confidence interval 95%	Number Of injection
8	520	0.16	520 ± 1.033	5
15	1520	0.18	1520 ± 2.288	8

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

Evaluation of the use of Ayah 6SX1-ST-2D- Solar cell CFI Analyser for the determination of Zn(II) in pharmaceutical preparation as an application

The adopted method was used for the determination of zinc (II) ion in two different company of pharmaceutical preparations(Zinc Sulphate, 45mg, Natra Health- UK and Zinc Sulphate,50 mg, Geri Care - New York) .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 incidentlight in addition to the classical method. A series of solutions were prepared of each pharmaceutical drug (0.6541 g, 0.1Mol.L⁻¹,100ml) (Zinc Sulphate, 45mg and Zinc Sulphate,50 mg) by transferring 1.5 mL to each of the five volumetric flask (25 mL), followed by the addition of gradual volumes of 0.1 Mol.L⁻¹ standard zinc (II)ion(0,1.5,1.75,2,2.25) ml which equivalent to (0,6,7,8,9) mMol.L⁻¹ in the case of use Ayah 6SX1-ST-2D Solar cell –CFI Analyzer, while transferring 0.25ml from 0.1 Mol.L⁻¹ pharmaceutical drug to each of the five volumetric flask (25 ml) , followed by the addition of gradual volumes of 0.1Mol.L⁻¹ standard zinc (II) ion (0,0.25,0.5,1,1.5) ml in order to have (0,1,2, 4,6) mMol.L⁻¹ in the case of use classical UV- spectrophotometric method . Flask no.1 is the sample .**Figure 10 A** shows the responses profile for this study.**Figure 10 B** ,Crepresented standard addition calibration graphs using Ayah 6SX1-ST-2D solar cell –CFI Analyser. **Table 10** sum up the summary of standard additions method results from the two samples with the amount of zinc (II) ion in pharmaceutical drug. While the data in **Table 11**sum up the results for two methods showing practical content of active ingredient at 95% confidence level , efficiency of determination and paired t-test for comparison at two different paths:

◆ Individual paired t-test

Comparison of newly developed method with official quoted value μ_o (45 mg or 50 mg) for Natra Health- UK and Geri Care - New York respectively as shown in**Table 11** by calculated t- values of each individual company and these comparison with tabulated t-value.

A hypothesis can be estimated as follow :

H_o (Null hypothesis) : for sample1: $\mu_o = \bar{w}_1$ for Natra Health- UK

for sample2: $\mu_o = \bar{w}_2$ for Geri Care - New York

i.e: There is no significant difference between the means of practical content for twodifferent companies (\bar{w}_i) and quoted value ($\mu_o=45$ mg or 50 mg)

Against

H_1 (alternative hypothesis) : $\mu_o \neq \bar{w}_i$ for two different companies

i.e:There is a significant difference between the quoted valueand means of practical content for two different companies

- From the results obtained that there $ist_{tab} > t_{value}$ at 95% confidence level for two drugs , which means no significant different between the quoted value (45 mg or 50 mg) and calculated t-value.

◆Secondary paired t-test

A paired t- test was conducted between the samplefrom twodifferent companies by development method of analysis (i.e: usingAyah 6SX1-ST-2DSolar cell CFI Analyser) with classical method (i.e: UV-Spectrophotometric)

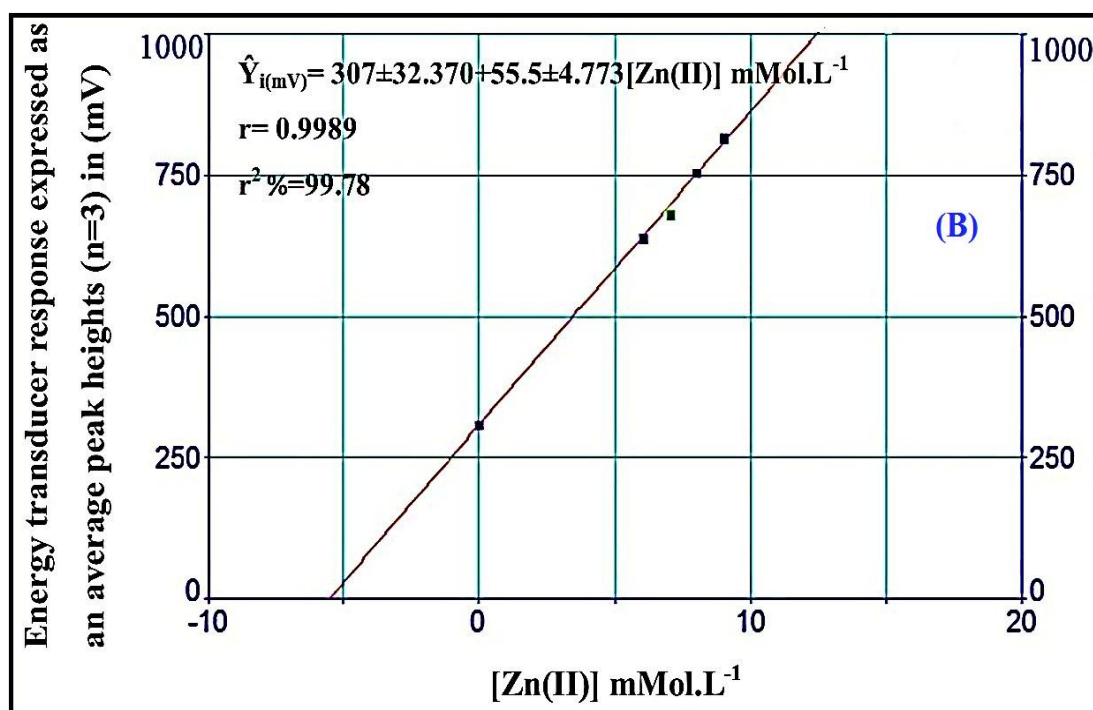
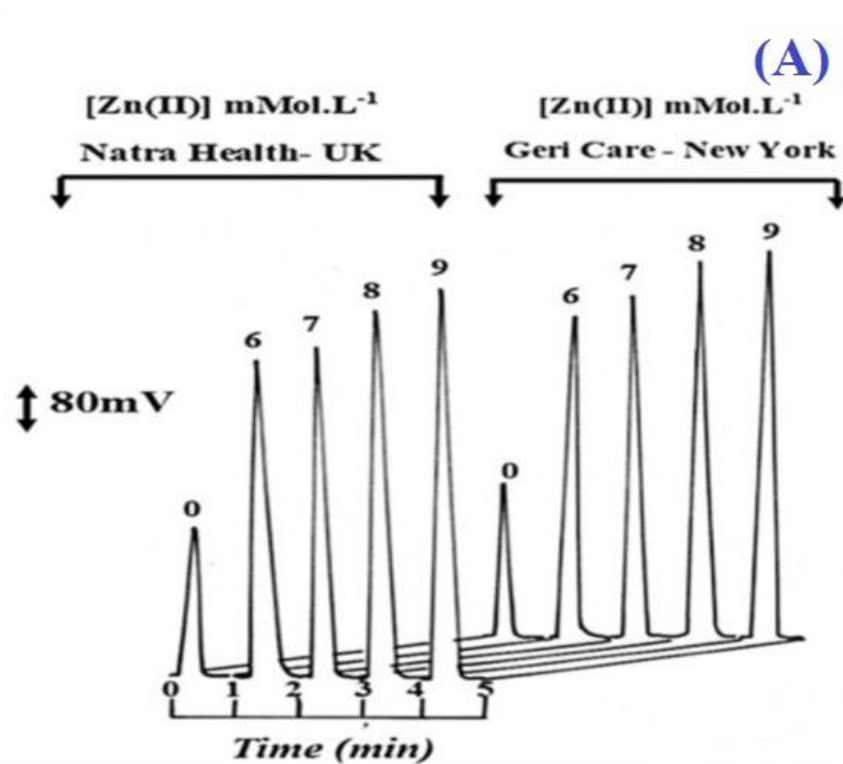
Taking into consideration a neglecting individual difference between one manufacturer and another.

A hypothesis can be estimated as a follow:

Null hypothesis H_o : $\mu_{Ayah\ 6SX1-ST-2D\ Solar\ cell\ CFI\ Analyzer} = \mu_{uv.sp}$

Against Alternative hypothesis H_1 : $\mu_{Ayah\ 6SX1-ST-2D\ Solar\ cell\ CFI\ Analyzer} \neq \mu_{uv.sp}$

Since calculation t-value of 16.142> $t_{tab}(12.71)$ at 95% confidence level. Therefore ; H_1 is accepted against H_o i.e: that there is a significant difference between two methods.



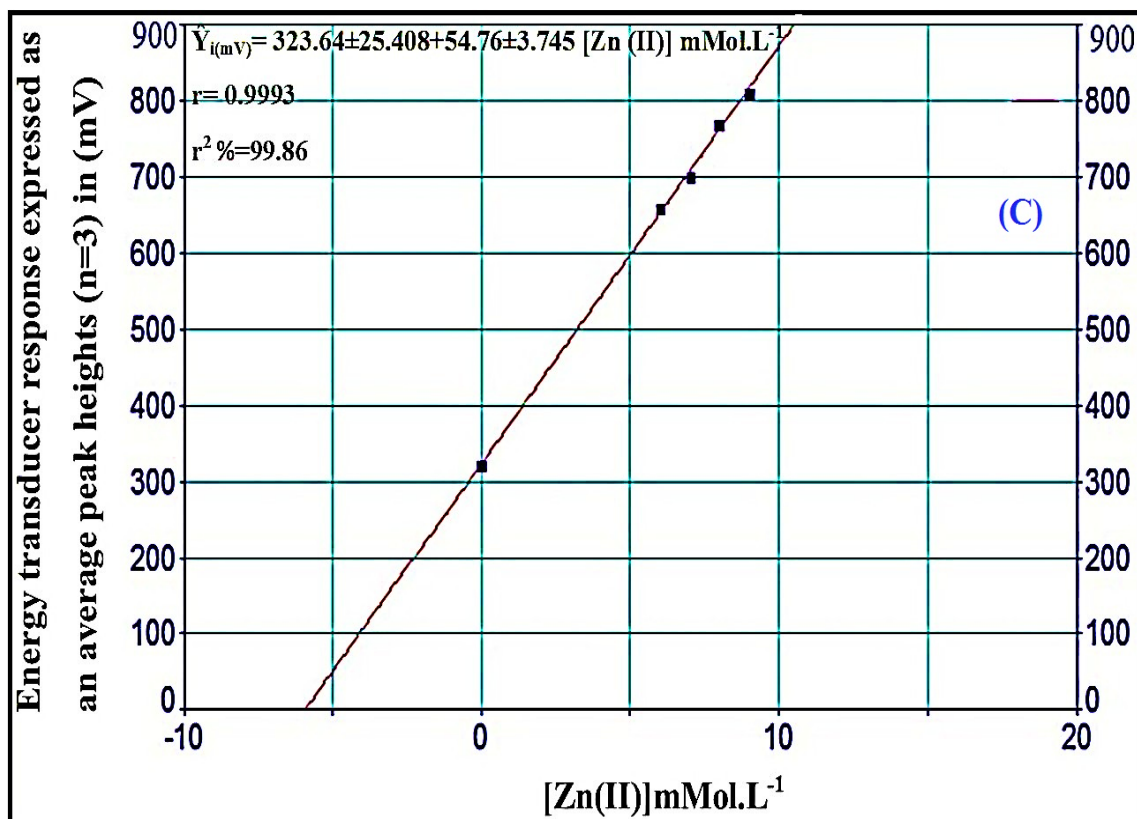


Fig. 10: Standard addition calibration graph for different samples using Ayah 6SX1-ST- 2Dsolar cell - CFI Analyser.

(A): Response profile verses time

(B): Zinc Sulphate, 45mg,NatraHealth,UK.

(C): Zinc Sulphate,50 mg,Geri Care , New York

Table 10: Results for the determination of Zinc (II) ion in pharmaceutical preparation by standard addition method using Ayah 6SX1-ST- 2D Solar cell CFI Analyser& Classical method (UV Spectrophotometric).

sample no	commercial name ,content ,company, country	Ayah 6SX1-ST-2D solar CFIa (mV)							Equation of standarad addition curve at 95% for n-2 $\hat{Y}_{i(mv)} = a \pm s_a t + b \pm s_b t [Zn(II)] \text{ mMol.L}^{-1}$ $\hat{Y}_i = a \pm s_a t + b \pm s_b t [Zn(II)] \text{ mMol.L}^{-1}$	r r^2 $r^2\%$	Practical conc. mMol.L ⁻¹	
		UV- SP. (classical method for absorbance measurement)									in 25 ml	in 25 ml
		[Zn(II)]mMol.L ⁻¹									in 100ml	in 100ml
		0	6	7	8	9						
		0	1	2	4	6						
1	ZincSulphate1250mg equivalent to 45mg zinc, NatraHealth, UK	310	640	680	755	815	307.0000±32.3700+55.5000±4.7730 [Zn(II)] mMol.L ⁻¹		0.9989 0.9978 99.78%	5.532	0.853	
		0.081	0.144	0.211	0.363	0.551	0.0667±0.0380+0.0782±0.0100[Zn(II)]mMol.L ⁻¹		0.9970 0.9940 99.40%	92.192	85.294	
2	ZincSulphate200mg Equivalent to 50 mg. zinc ,Geri Care , New York	322	659	700	770	810	323.6400±25.4080+54.7600±3.7450 [Zn(II)] mMol.L ⁻¹		0.9993 0.9986 99.86%	5.910	0.915	
		0.095	0.148	0.221	0.363	0.577	0.0731±0.0600+0.0799±0.0190[Zn(II)] mMol.L ⁻¹		0.9929 0.9858 98.58%	98.509	91.489	

\hat{Y}_i^* = estimated value for absorbance, r = Correlation coefficient , r^2 = coefficient of determination (C.O.D), $r^2\%$ = Linearity percentage

Table 11: Summary of data for paired t-test, practical content and efficiency of determination of Zn(II) in two samples of pharmaceutical preparation

Sample no	Confidence interval for the average weight of tablets $\bar{w}_i \pm 1.96 \sigma_{n-1} / \sqrt{n}$ at 95% (g)	Theoretical content for the active ingredient $\bar{w}_i \pm 1.96 \sigma_{n-1} / \sqrt{n}$ at 95% (mg)	Sample weight equivalent to 0.6541 g (100 mMol.L ⁻¹) of the active ingredient w_i (g)	Practical content of active ingredient		Efficiency of determination (Rec%)	Paired t-test			
				In 100 ml of sample $\bar{w}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$ at 95%, (g)	in tablets $\bar{w}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$ at 95%, (mg)		Individual comparison ($\bar{w}_i - \mu_0$) \sqrt{n} / σ_{n-1} Ayah 6SX1-ST-2 D Solar cell- CFI Analyser with Quoted value $t_{0.05/2, 2} = 4.303$	Comparison between two method		
				Ayah 6SX1-ST-2D solar CFIa (mV) UV- SP. (classical method for absorbance measurement)				Xd	\bar{X}_d (σ_{n-1})	$t_{cal} = \frac{\bar{X}_d \sqrt{n}}{\sigma_{n-1}}$ at 95 %
1	0.5932±0.0013	45±0.0986	8.6225	0.6030±0.062	41.486±4.266	92.19%	-3.545 << 4.303	3.10	3.310290	12.71
				0.5579±0.099	38.382±6.811	85.29%				
2	0.4298±0.0028	50±0.3257	5.6226	0.6443±0.032	49.251±2.446	98.50%	-1.317 << 4.303	3.51		16.142
				0.5984±0.055	45.744±4.204	91.49%				

Xd: Difference between two method , \bar{X}_d : difference mean , σ_{n-1} : Difference standard deviation , n=3 for individual & n=2 for comparison between two method.

CONCLUSION

The proposed turbidmetric flow-injection method is simple, rapid, inexpensive and sensitive for the determination of Zn (II) ion. The method based on reaction between Zn (II) ion with mefenamic acid in aqueous medium to form yellow precipitate as ion pair complex. The new method can be used to determine of Zn (II) ion in pure and pharmaceutical preparation. The precipitate is measured via the reflection of incident light. The %R.S.D was <0.2% and good agreements were observed for all samples, which is an indication of satisfactory accuracy of the proposed method. The standard additions method was used to avoid matrix effects.

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