



## A New Approach for the Turbidimetric Determination of Hydronium ion by Using Homemade Linear Array Ayah 5SX1-T-1D-CFI Analyser

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### Abstract

A new Turbidimetric method characterized by simplicity, accuracy and speed for determination of Hydronium ion by continuous flow injection analysis. The method was based on the formation of complex  $Zn_3[Fe(CN)_6]$  for Zinc(II) that was eluted by Hydronium ion from cation exchanger column with Potassium hexacyanoferrate(III) for the formation of a pale yellow precipitate and this precipitate was determined using homemade Linear Array Ayah-5SX1-T-1D continuous flow injection analyser. The optimum parameters were  $2.7 \text{ mL}\cdot\text{min}^{-1}$  flow rate using  $H_2O$  as a carrier stream,  $1.7 \text{ mL}\cdot\text{min}^{-1}$  reagent stream,  $110 \mu\text{L}$  sample volume and open valve for the purge of the sample segment. Data treatment shows that linear range  $0.01\text{-}0.1 \text{ mol}\cdot\text{L}^{-1}$  for each acids ( $HClO_4, HNO_3, HCl, H_2SO_4$ ) while L.O.D  $30, 50.01, 29.75, 51.41 \mu\text{g}/\text{sample}$  for  $HClO_4, H_2SO_4, HCl, HNO_3$  respectively from the stepwise dilution for minimum concentration of lowest concentration in linear dynamic range of the calibration graph. The correlation coefficient ( $r$ ) was  $0.9891, 0.9930, 0.9917, 0.9940$  while percentage linearity ( $\%r^2$ ) was  $97.85\%, 98.81\%, 98.61\%, 98.36\%$  for  $HClO_4, H_2SO_4, HCl, HNO_3$  respectively. R.S.D. % for the repeatability ( $n=5$ ) was  $< 2\%$  for determination of Hydronium ion with concentration  $20$  and  $80 \text{ mMol}\cdot\text{L}^{-1}$ . The method was applied successfully for the determination of Hydronium ion in commercial samples. Using paired t-test between the newly developed method and classical method; shows that there were no significant differences between either methods. On this basis the new method can be accepted as an alternative analytical method for determination of Hydronium ion in commercial samples.

**Keywords:** Hydronium ion, ion exchange, turbidimetric, flow injection analysis.

## نمط جديد لقياس التعكيرية لتقدير ايون الهيدرونيوم باستخدام محلل الحقن الجرياني المستمر Linear Array Ayah 5SX1-T-1D-CFI Analyser المصنوع محلياً

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### الخلاصة

استحدثت طريقة بسيطة وسريعة ودقيقة لتقدير ايون الهيدرونيوم من خلال اقتران الحقن الجرياني المستمر مع قياس التعكيرية. تستند الطريقة على تكوين معقد راسب من  $Zn_3[Fe(CN)_6]$  للزنك (II) المزاح بواسطة ايون الهيدرونيوم من عمود المبادل الايوني مع الكاشف سداسي سيانات الحديد(III) البوتاسيوم، اذ ينتج راسب

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اصفر شاحب، قدر الراسب المتكون باستخدام جهاز محلل الحقل الجرياني المستمر Ayah 5SX1-T- 1D المصنوع محلياً. درست الظروف المثلى للتفاعل، اذ استخدم 2.7 مل. دقيقة<sup>-1</sup> كسرعة جريان للتيار ناقل H<sub>2</sub>O، 1.7 مل. دقيقة<sup>-1</sup> كسرعة جريان للتيار الكاشف، واستخدم 110 مايكرو لتر كحجم لامتداد المحقن مع ترك صمام الحقن مفتوح لخروج مقطع النموذج. بينت معالجة البيانات المستحصلة المدى الخطي 0.01-0.1 مول. لتر<sup>-1</sup> لكل حامض (HClO<sub>4</sub>, HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>) بينما حدود الكشف 30، 50.01، 29.75، 51.41 مايكروغرام/امتداد لكل من (HClO<sub>4</sub>, HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>) على التوالي من التخفيف التدريجي لاقل تركيز في منحنى المعايرة. معامل الارتباط (r) 0.9891، 0.9930، 0.9917، 0.9940، والنسبة المئوية للخطية هي 97.85 %، 98.81 %، 98.61 %، 98.36 % لكل من (HClO<sub>4</sub>, HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>) على التوالي. الانحراف القياسي النسبي المئوي (n=5) اقل من 2% لتكيزين 20 و 08 ملي مول. لتر<sup>-1</sup> لمحلول ايون الهيدرونيوم. طبقت الطريقة لتقدير ايون الهيدرونيوم في النماذج التجارية. استخدام اختبار t-المزدوج لاجراء مقارنة بين الطريقة المستحدثة والطريقة القياسية (PH meter)، وجد انه لا يوجد فرق جوهري بين الطريقتين وبذلك يمكن استخدام الطريقة المستحدثة كطريقة بديلة لتقدير ايون الهيدرونيوم في النماذج التجارية.

## 1. Introduction

Acids play important roles in the human body. Hydrochloric acid present in the stomach this aids in digestion by breaking down large and complex food molecules. Amino acids are required for synthesis of proteins required for growth and repair of body tissues. Fatty acids are also required for growth and repair of body tissues. Nucleic acids are important for the manufacturing of DNA and RNA and transmitting of traits to offspring through genes. Carbonic acid is important for maintenance of pH equilibrium in the body. An acid (from the Latin acidus/acēre meaning sour is a chemical substance whose aqueous solutions are characterized by a sour taste, the ability to turn blue litmus red, and the ability to react with bases and certain metals (like calcium) to form salts. Aqueous solutions of acids have a pH of less than 7. A lower pH means a higher acidity, and thus a higher concentration of hydrogen ions in the solution [1-5]. Chemicals or substances having the property of an acid are said to be acidic. Acids are used as additives to drinks and foods, as they alter their taste and serve as preservatives. Phosphoric acid, for example, is a component of cola drinks. Acetic acid is used in day to day life as vinegar. Carbonic acid is an important part of some cola drinks and soda. Citric acid is used as a preservative in sauces and pickles. There are numerous uses for acids. Acids are often used to remove rust and other corrosion from metals in a process known as pickling [6,7]. They may be used as an electrolyte in a wet cell battery, such as sulfuric acid in a car battery. Strong acids, sulfuric acid in particular, are widely used in mineral processing. For example, phosphate minerals react with sulfuric acid to produce phosphoric acid for the production of phosphate fertilizers, zinc is produced by dissolving zinc oxide into sulfuric acid [8], purifying the solution. In the chemical industry, acids react in neutralization reactions to produce salts. For example, nitric acid reacts with ammonia to produce ammonium nitrate, a fertilizer. Additionally, carboxylic acids can be esterified with alcohols, to produce esters. Some of the most commonly used methods for determination of acid (H<sub>3</sub>O<sup>+</sup>) include spectrophotometry [9,10], atomic absorption spectrophotometry [11], flow injection method [12,13], Microwave [14,15], HPLC [16], chemiluminescence [17]. This work, describes a simple turbidimetric flow injection method that have been developed for the determination of Hydronium ion. The method is based on the reaction between eluted zinc by Hydronium ion from cation exchange column packed with potassium hexacyano ferrate (III) K<sub>3</sub>[Fe(CN)<sub>6</sub>] to form yellow precipitate.

## 2. Experimental

### 2.1 Chemicals & Reagents

All chemicals were used of analytical reagent grade while distilled water was used to prepare the solution. A standard solution of zinc acetate Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O. (BDH, 0.3 mol.L<sup>-1</sup>) was prepared by dissolving 6.585 g in 100 mL distilled water. A stock solution of potassium hexacyano ferrate (III) K<sub>3</sub>[Fe(CN)<sub>6</sub>] was prepared by dissolving 32.926 g in 500 mL of distilled water. Sulfuric Acid solution (96%, 1.84 g.mL<sup>-1</sup>, BDH, 2 mole.L<sup>-1</sup>) was prepared by pipetting 222.09 mL of concentrated sulfuric acid and complete the volume with distilled water to 2000 mL of volumetric flask. Hydrochloric Acid solution (38%, 1.19 g.mL<sup>-1</sup>, BDH, 2 mole.L<sup>-1</sup>) was prepared by pipetting 323 mL of concentrated

Hydrochloric acid and complete the volume with distilled water to 2000 mL of volumetric flask. Perchloric acid solution (60%,  $1.54 \text{ g.mL}^{-1}$ , BDH,  $2 \text{ mole.L}^{-1}$ ) was prepared by pipetting 435.25 mL of concentrated Perchloric acid and complete the volume with distilled water to 2000 mL of volumetric flask. Nitric Acid solution (70%,  $1.42 \text{ g.mL}^{-1}$ , BDH,  $2 \text{ mole.L}^{-1}$ ) was prepared by pipetting 253.64 mL of concentrated Nitric acid and complete the volume with distilled water to 2000 mL of volumetric flask. Each acids was standardized against Sodium Carbonate  $\text{Na}_2\text{CO}_3$  Solution (BDH,  $2 \text{ mol.L}^{-1}$ ).

## 2.2 Preparation of column

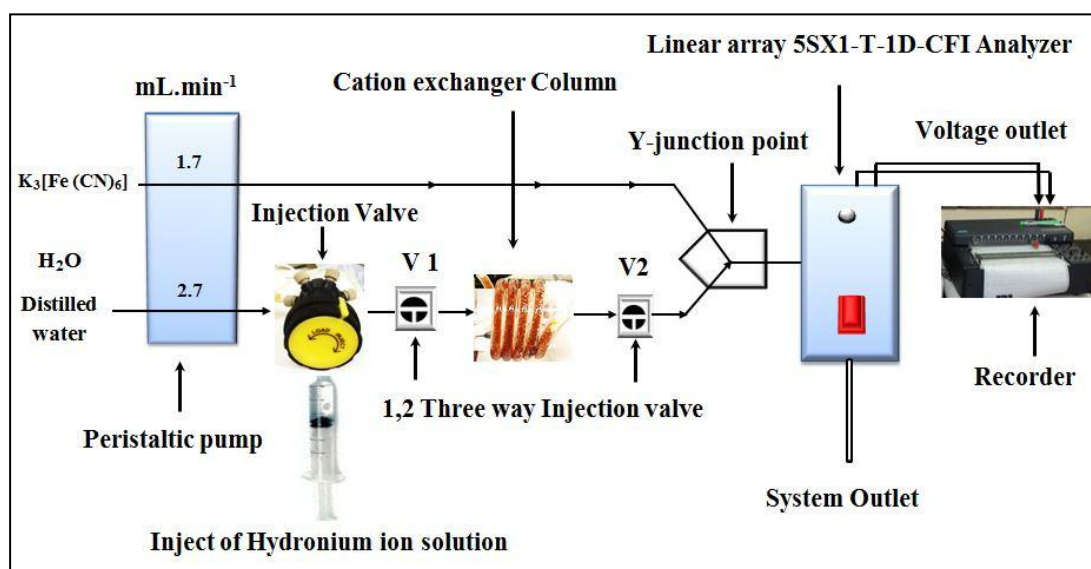
Few grams of strong cation exchange resin (amber lite 120) was taken and washed with distilled water to remove any fine solid particles that may be present in the bulk of the resin due to crashed resin beads, followed by washing with concentrate HCl in order to convert cationic exchange resin to  $\text{H}^+$  form; followed by constant wash with distilled water to remove excess acids that may present in the resin beads, until a negative test for the eluted liquid with blue litmus paper the resin. The resin in this form is ready for use.

## 2.3 Preparation of the resin for termination of acids

A saturated solution of zinc acetate is prepared in a beaker followed by passage of this saturated solution (after decantation) the color of resin is changed gradually by the replacement of H ion with Zinc ion(II). This process should be continuous until there is a positive test that zinc ion (II) is discharged from the column. This indicates that the exchange has been completed. The hole process is followed by washing the column with distilled water until a negative test for zinc is a achieved. At this point the resin is ready for use for the measurements throughout this research work.

## 2.4 Apparatus and Manifold

Homemade instrument Linear Array Ayah 5SX1-T-1D-CFI analyzer [18] using five super snow white Light Emitting Diode (LED) as a source with a solar cell as a detector. It's used for measurement of attenuation of incident light. Two channels of variable speeds Peristaltic pump (Ismatec type ISM796), A rotary 6-port injection valve (Rheodyne, U.S.A) with a sample loop (0.5 mm i.d, Teflon, variable length) used for sample injection. The output signals was recorded by x-t potentiometric recorder (KOMPENSO GRAPH C-1032) Siemens (Germany) and Digital AVO-meter (auto range) (0.00-2000 mV) (China). Peak height was measured for each signal. Figure-1 shows the flow gram that was used for the determination and detection Hydronium ion.

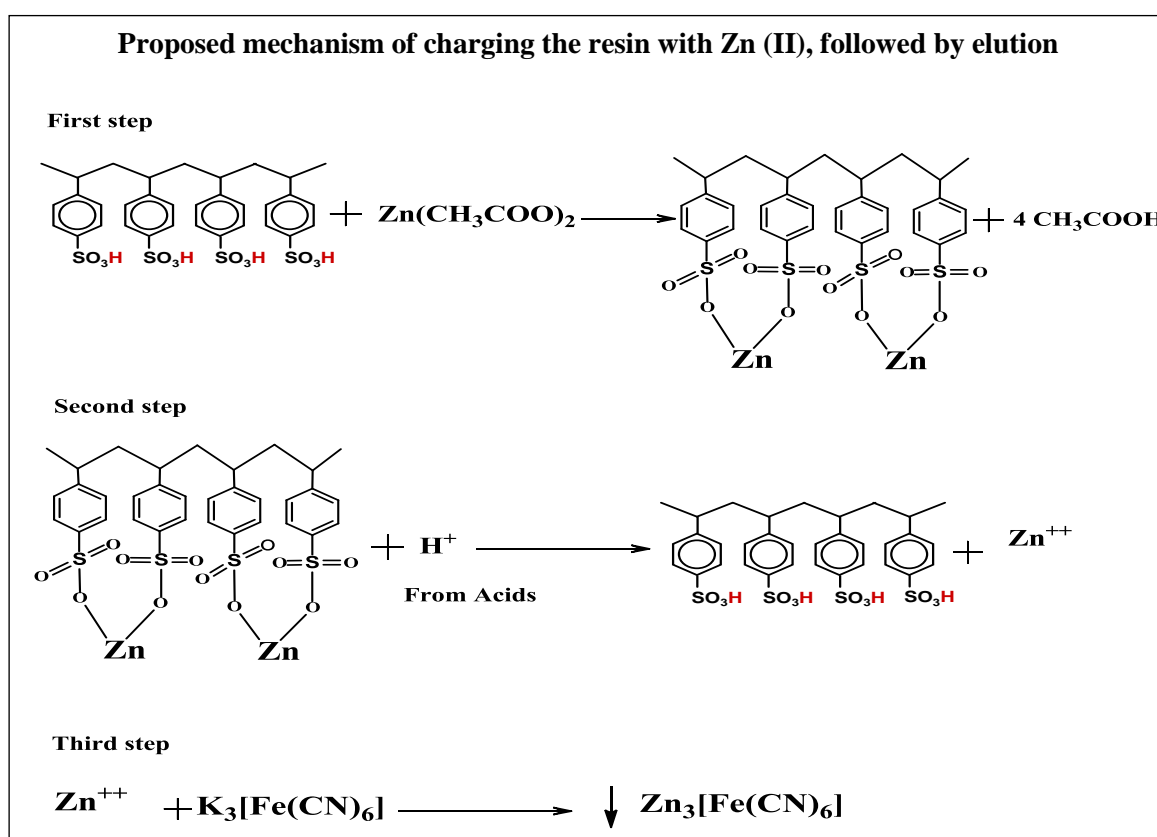


**Figure 1-** Schematic diagram of flow injection analysis system used for determination of Hydronium ion,  $V_1$  and  $V_2$  three way injection valves.

## 2.5 Methodology

The flow diagram shown in figure-1, for determination of Hydronium ion, by the reaction between potassium hexacyanoferrate(III) and Zinc (II) ion that eluted from cation exchange Column by Hydronium ion to form yellow precipitate from complex  $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  which is composed of two lines : the first line is the carrier stream (distilled water) at  $2.7 \text{ ml.min}^{-1}$  flow rate which passes to

injection valve to carry Hydronium ion sample (110  $\mu\text{L}$ ) then passes through cation exchange Column to elute the zinc; while the second line is the reagent stream supplies  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution ( $0.1 \text{ mol.L}^{-1}$  for  $(\text{HCl}, \text{H}_2\text{SO}_4)$  &  $0.04 \text{ mol.L}^{-1}$  for  $(\text{HNO}_3, \text{HClO}_4)$  respectively) at  $1.7 \text{ mL.min}^{-1}$ . Both line meet at a junction (Y-junction), with an outlet for reactants product from  $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  complex, which passes through a Homemade instrument Linear Array Ayah 5SX1-T-1D-CFI analyzer that works with a five snow white light emitting diode will be used as a source. Each solution injected was assayed in triplicate. The responses was recorded on x-t potentiometric recorder to measurement the turbidity via the reflection & attenuation light that collides on the surfaces of precipitated particles  $0-180^\circ$ . A proposed mechanism of charging the resin with Zn (II) ion followed by elution shown in scheme-1.



**Scheme 1-** Proposed mechanism for  $\text{Zn}_3[\text{Fe}(\text{CN})_6]$  complex formation.

### 3. Results and Discussion

#### 3.1 Study of the optimum parameters :-

The flow gram shown in show figure-1 was investigated for the relation of chemical and physical variables, in order to obtained the optimum conditions for system. They were optimized by making all variables constant and varying one at each time.

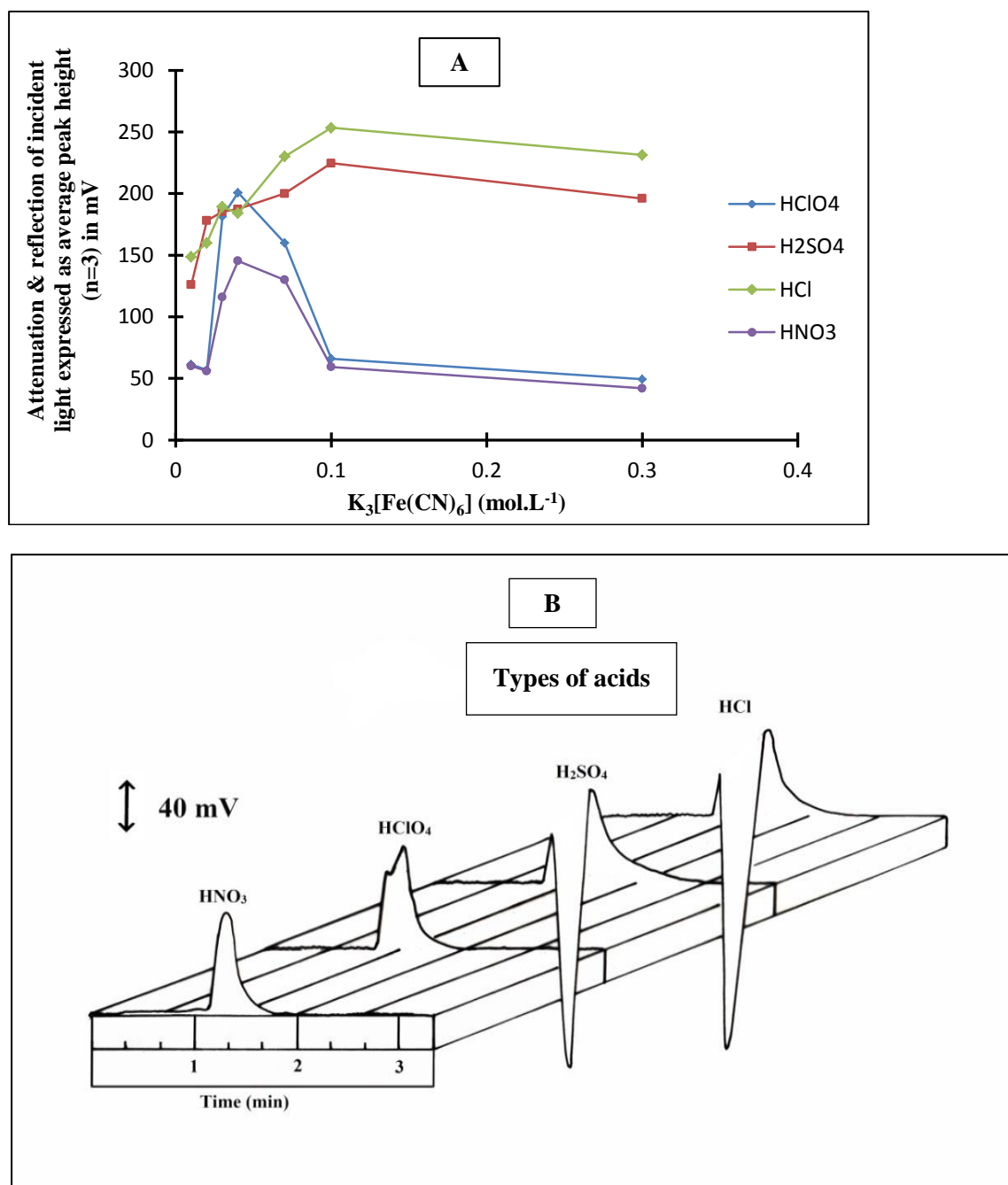
##### 3.1.1 Chemical Variables

###### • 3.1.1.1 Effect of $\text{K}_3[\text{Fe}(\text{CN})_6]$ Concentration:-

Using the preliminary experiment parameters of Hydronium ion  $0.1 \text{ mol.L}^{-1}$ , intensity of incident light of LED,  $0.7 \text{ V}$ , flow rate of carrier stream and reagent stream  $2.7 \text{ mL.min}^{-1}$  and  $1.7 \text{ mL.min}^{-1}$  respectively with  $80 \mu\text{L}$  sample volume and allowed permissible time for sample injection of 30 seconds (open valve mode). A study was conducted to optimize the preferred concentration of potassium hexacyano ferrate(III) in the range of  $0.01$  to  $0.3 \text{ mole.L}^{-1}$  for each acids that can be used for formation a yellow precipitate of  $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  by eluted zinc (II) ion from the cationic exchange column. Table-1 summarizes the data obtained showing the average of the three successive readings, standard deviation, relative standard deviation and the confidence interval of the average responses at 95% confidence ( $\alpha=0.05$ ).

Figure-2-A shows Effect of potassium hexacyano ferrate (III)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  concentration on attenuation of incident light expressed as peak height ( $n=3$ ) for Hydronium ion. From the results

obtained it was noticed that the optimum potassium hexacyano ferrate (III) concentration was  $0.1 \text{ mol.L}^{-1}$  for ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ) &  $0.04 \text{ mol.L}^{-1}$  for ( $\text{HNO}_3$ ,  $\text{HClO}_4$ ) respectively. It was noticed that there is an increase in the response of the precipitated complex with increasing potassium hexacyano ferrate (III) concentration. While an increase in hexacyano ferrate (III) concentration Higher than  $0.1 \text{ mol.L}^{-1}$  for ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ) &  $0.04 \text{ mol.L}^{-1}$  for ( $\text{HNO}_3$ ,  $\text{HClO}_4$ ) respectively leads to a significant differences in the response. This might be due to increase in amount of precipitate, thus leading to a decrease in reflection & attenuation of light; this causes a decrease in peak height resulting from measurement. Therefore,  $0.1 \text{ mol.L}^{-1}$  for ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ) &  $0.04 \text{ mol.L}^{-1}$  for ( $\text{HNO}_3$ ,  $\text{HClO}_4$ ) respectively was chosen as an optimum concentration for the precipitation. Figure-2-B shows the response-time profile of the optimum results for each acids ( $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) as it was obtained from Linear Array Ayah 5SX1-T-1D-CFI analyzer.



**Figure 2-** Effect of hexacyano ferrate (III)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  concentration ( $\text{mol.L}^{-1}$ ) on, (A): Attenuation & reflection of incident light in mV for Hydronium ion ( $0.1 \text{ mol.L}^{-1}$ )  $80 \mu\text{L}$ , flow rate of carrier stream and reagent stream  $2.7$  and  $1.7 \text{ ml.min}^{-1}$  respectively, (B): Response profile.

**Table 1-** Effect of concentration change of  $K_3[Fe(CN)_6]$  on measurement of incident light for determination Hydronium ion.

Type of Acids	Data output	Conc. of $K_3[Fe(CN)_6]$ (Mol.L <sup>-1</sup> )						
		0.01	0.02	0.03	0.04	0.07	0.1	0.3
HClO <sub>4</sub>	Average Response (mV)	61.33	56.66	181.33	200.66	160	66	49.33
	$\sigma_{n-1}$	2.30	1.15	2.30	1.15	0	0	1.15
	R.S.D %	3.76	2.03	1.27	0.57	0	0	2.34
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	61.33±5.73	56.66±2.86	181.33±5.73	200.66±2.8	160±0	66±0	49.33±2.86
H <sub>2</sub> SO <sub>4</sub>	Average Response (mV)	126	178	185.33	187.33	200	224.66	196
	$\sigma_{n-1}$	2	3.46	4.61	6.11	0	2.30	3.46
	R.S.D %	1.58	1.94	2.49	3.26	0	1.02	1.76
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	126±4.96	178±8.60	185.33±11.4	187.3±15.1	200±0	224.66±5.7	196±8.60
HCl	Average Response (mV)	148.66	160	189.33	184	230	253.33	231.33
	$\sigma_{n-1}$	4.16	0	5.03	2	0	1.15	7.02
	R.S.D %	2.80	0	2.65	1.08	0	0.45	3.03
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	148.66±10.34	160±0	189.33±12.5	184±4.96	230±0	253.33±2.8	231.33±17.4
HNO <sub>3</sub>	Average Response (mV)	60	56	116	145.33	130	59.33	42
	$\sigma_{n-1}$	0	2	0	1.154	0	1.15	0
	R.S.D %	0	3.57	0	0.79	0	1.94	0
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	60±0	56±4.96	116±0	145.33±2.86	130±0	59.33±2.86	42±0

### 3.1.2 Physical Variables

#### • 3.1.2.1 Variation of Incident Light Intensity

A variable intensity of white LEDs light source expressed in V (0.2-2) was used for this study, and the system used for determination of Hydronium ion (0.05 mol.L<sup>-1</sup> for all physical parameters) for each acids via formation of a yellow precipitate, 80  $\mu$ L sample volume and optimum concentration of  $K_3[Fe(CN)_6]$  [ 0.1 mol.L<sup>-1</sup> for HCl, H<sub>2</sub>SO<sub>4</sub> & 0.04 mol.L<sup>-1</sup> for HClO<sub>4</sub>, HNO<sub>3</sub>] respectively for each acids. The obtained results tabulated in table-2 showing the average of the three successive readings, standard deviation, relative standard deviation and the confidence interval of the average responses at 95% confidence( $\alpha=0.05$ ).

It was noticed that an increase in the attenuation of incident light results increase in response. While an increase in intensity higher than 1.8 V leads to a significant difference in the response. This might be due to transparency effect of the fine particle with increase of incident power of radiation. This effect can be distributed to a prominent fine particle that is formed. The intensity of 1.8 V was selected as the optimum voltage output that can be supplied to give a better response for each acids. Figure-3 shows the plot of attenuation of incident light vs. change in intensity of incident light.

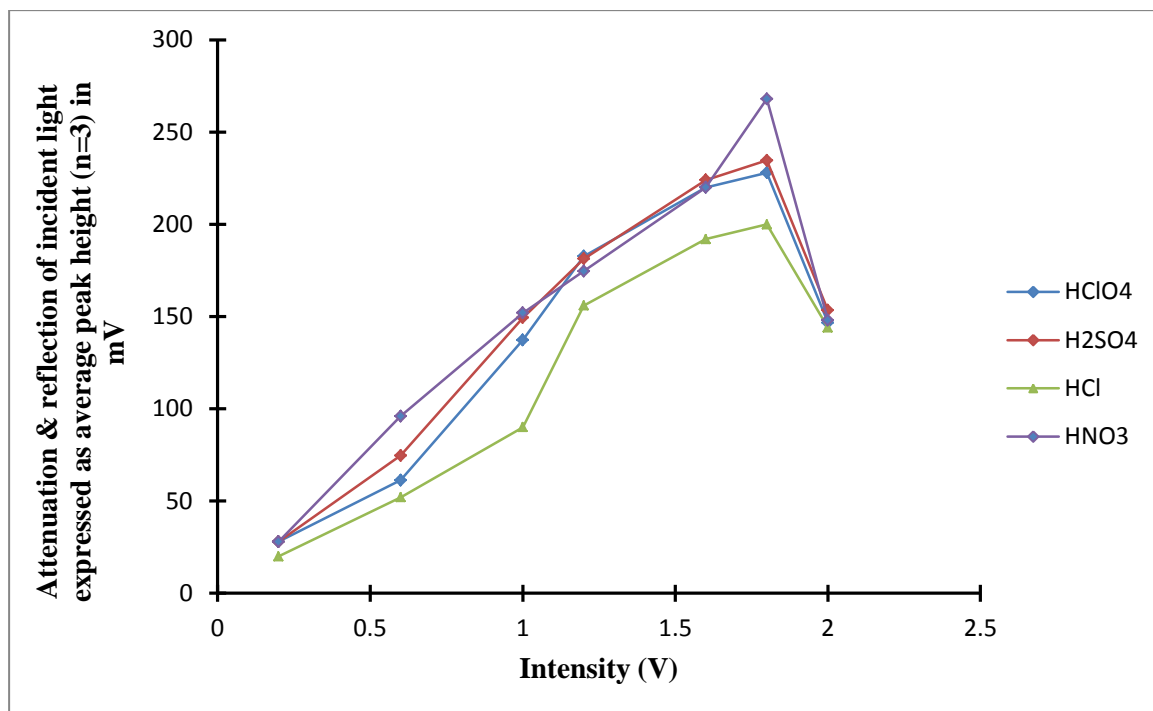


Figure 3- Variation of incident light vs. light intensity expressed in V.

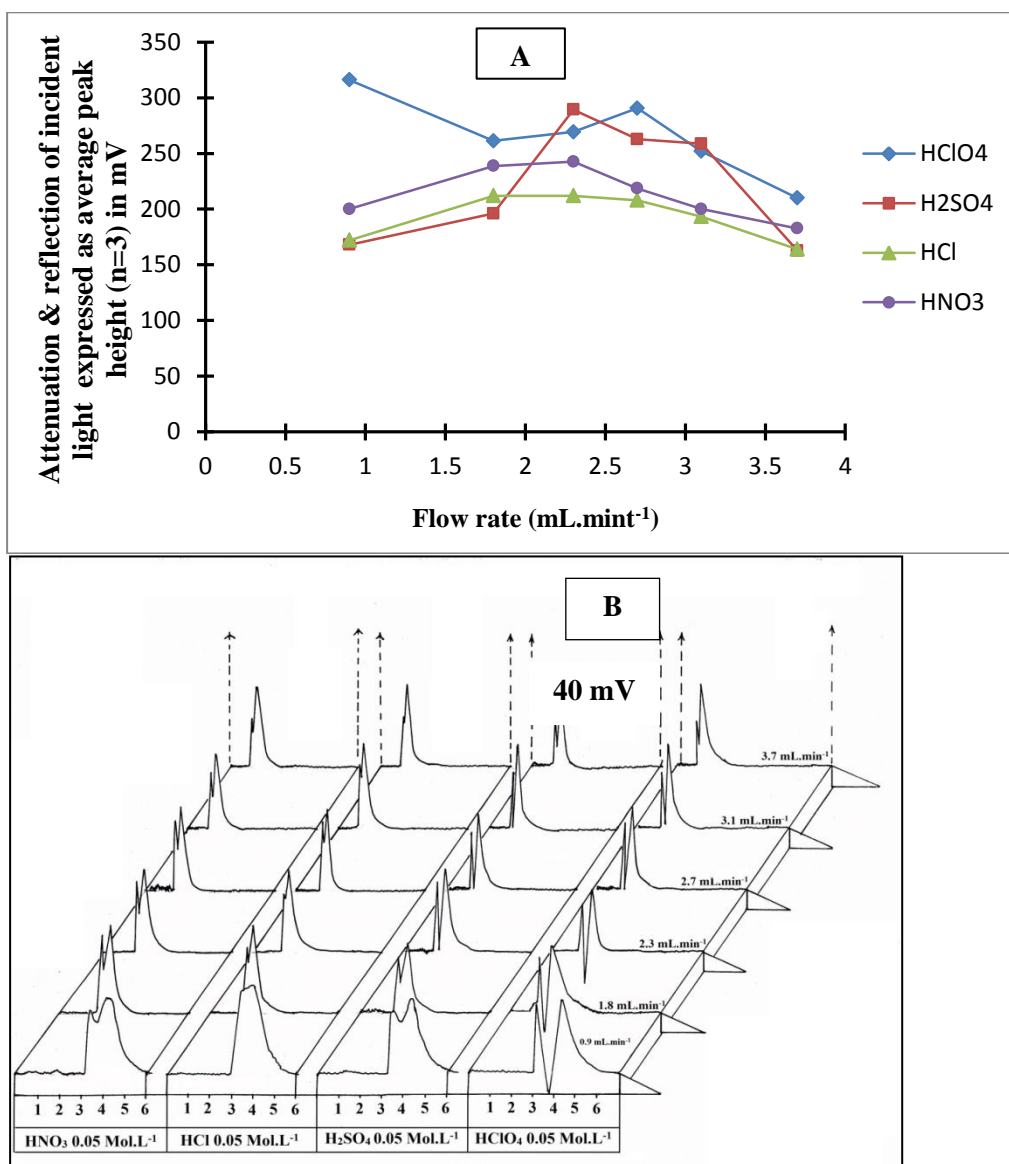
Table 2- Effect light intensity on the measurement of light attention for determination Hydronium ion.

Type of Acid	Data output	Intensity (V)						
		0.2	0.6	1	1.2	1.6	1.8	2
HClO <sub>4</sub>	Average Response (mV)	28	61.33	137.33	182.66	220	228	146.6
	$\sigma_{n-1}$	0	2.30	2.30	2.30	0	0	2.30
	R.S.D %	0	3.76	1.68	1.26	0	0	1.57
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	28±0	61.33±5.73	137.33±5.73	182.66±5.73	220±0	228±0	146.6 ± 5.73
H <sub>2</sub> SO <sub>4</sub>	Average Response (mV)	28	74.66	149.33	181.33	224	234.66	153.33
	$\sigma_{n-1}$	0	2.30	4.61	2.30	6.92	2.30	2.30
	R.S.D %	0	3.03	3.09	1.2	3.09	0.9	1.50
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	28±0	74.66±5.73	149.33±11.47	181.33±5.73	224±17.21	234.66±5.7	153.33±5.73
HCl	Average Response (mV)	20	52	90	156	192	197.33	144
	$\sigma_{n-1}$	0	0	0	0	0	4.61	0
	R.S.D %	0	0	0	0	0	2.34	0
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	20±0	53±0	90±0	156±0	192±0	197.33±11.4	144±0
HNO <sub>3</sub>	Average Response (mV)	28	96	152	174.66	220	268	148
	$\sigma_{n-1}$	0	4	0	4.61	0	6.92	0
	R.S.D %	0	4.16	0	2.64	0	2.58	0
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	28±0	96±9.93	152±0	174.66±11.47	220±0	268±17.21	148±0

### • Effect of Flow Rate

A set of experiments were conducted for the optimization of the preferred flow rate ( $0.9\text{--}3.7\text{ mL}\cdot\text{min}^{-1}$ ) using the optimum concentration of potassium hexacyanoferrate(III), achieved in previous section. Table-3 summarizes the results obtained, include the average of three successive readings, the arrival time of sample segment to the flow measuring cell (sec) and the base width of response  $\Delta t_B$  (min).

It was noticed from the results obtained that there were no significant differences in the response height at low flow rate ( $<1.8\text{ mL}\cdot\text{min}^{-1}$ ) even the response show a wider base width (increase analysis time) as shown in figure-4-A. This might be attributed to the dilution of the sample segment due to dispersion region surrounding the central part of the segment and the central dispersion due to diffusion and convection. Also, It was noticed that at flow rate higher than  $2.7\text{ mL}\cdot\text{min}^{-1}$  (decrease analysis time) there were a small decrease in the response in spite of obtaining sharp response maximum. This may be due to the increased speed rate of the reaction and therefore remove a small amount of zinc to form precipitate, or unavailability of enough time for the response measurement before it's departure of the measuring cell at a short time. On this basis a compromise was made between the height of response and the analysis time, therefore, a flow rate of carrier stream  $2.7\text{ mL}\cdot\text{min}^{-1}$  and  $1.7\text{ mL}\cdot\text{min}^{-1}$  of reagent stream were chosen as optimum flow rate throughout this work. Figure-4-B shows the response-time profile of results for each acids ( $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) as it was obtained from Linear Array Ayah 5SX1-T-1D-CFI analyzer.



**Figure 4-** Effect of variation of flow rate ( $\text{mL}\cdot\text{min}^{-1}$ ) on, (A) Attenuation & reflection of incident light expressed as peak height ( $n=3$ ) in mV, (B) Response profile.



**Table 3-** Effect flow rate on the measurement of light attention for determination Hydronium ion.

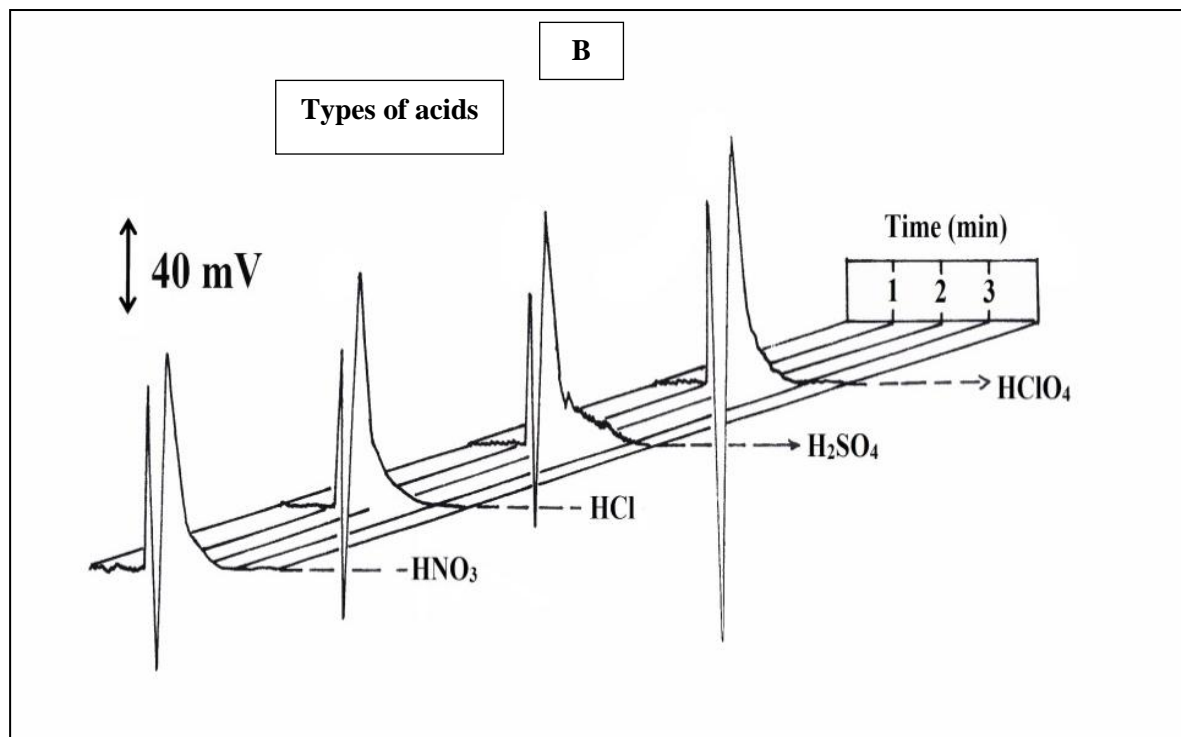
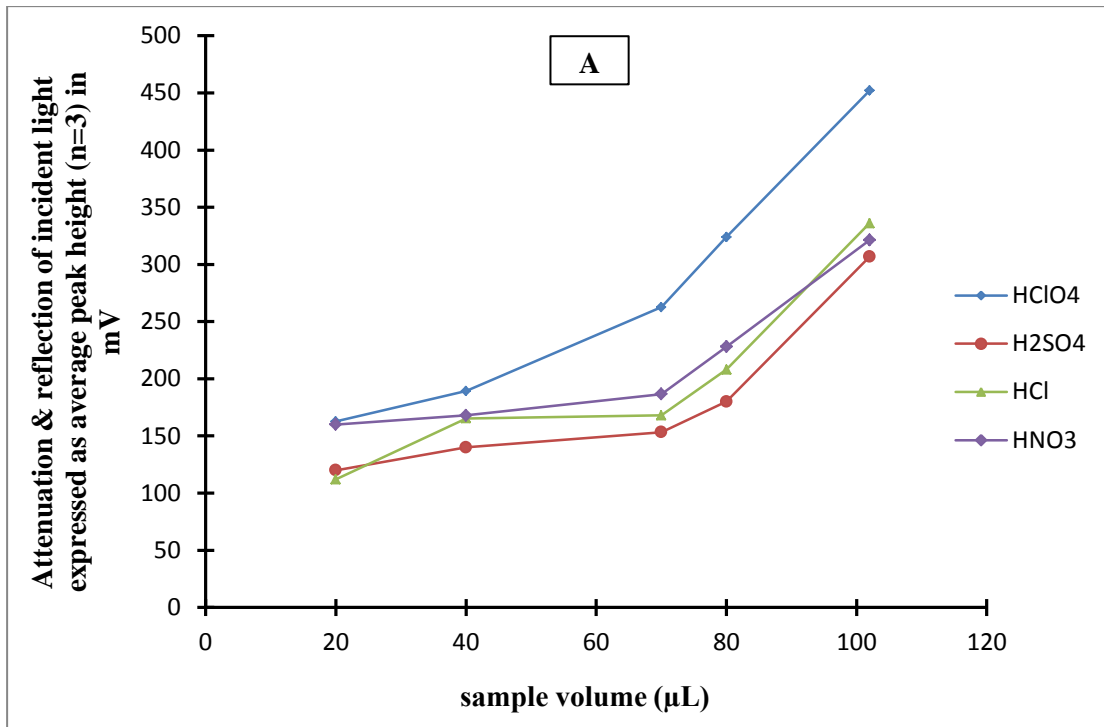
Type of Acid	Data output	Flow Rate (mL.mint <sup>-1</sup> )					
		0.9	1.8	2.3	2.7	3.1	3.7
		0.6	1.2	1.5	1.7	2	2.3
HClO <sub>4</sub>	Average Response (mV)	316	261.33	269.33	290.66	252	210.66
	$\sigma_{n-1}$	0	4.61	9.23	2.30	6.92	2.30
	R.S.D %	0	1.76	3.42	0.79	2.74	1.09
	Confidence interval of the mean $\bar{y}_i \pm t_{0.05, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	316±0	261.33±11.47	269.33±22.9	290.66±5.73	252±17.21	210.66±5.7
	t	408	240	180	150	150	138
	$\Delta t_B$	180	120	90	60	84	78
H <sub>2</sub> SO <sub>4</sub>	Average Response (mV)	168	196	289.33	262.66	258.66	162.66
	$\sigma_{n-1}$	0	0	2.30	2.30	2.30	4.61
	R.S.D %	0	0	0.79	0.87	0.89	2.83
	Confidence interval of the mean $\bar{y}_i \pm t_{0.05, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	168±0	196±0	289.33±5.73	262.66±5.73	258.66±5.73	162.6±11.4
	t	408	210	210	162	150	132
	$\Delta t_B$	132	78	96	72	90	60
HCl	Average Response (mV)	172	212	172	208	193.33	164
	$\sigma_{n-1}$	0	0	0	0	2.30	0
	R.S.D %	0	0	0	0	1.19	0
	Confidence interval of the mean $\bar{y}_i \pm t_{0.05, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	172±0	212±0	172±0	208±0	193.33±5.73	164±0
	t	408	222	210	156	168	144
	$\Delta t_B$	120	90	90	66	90	60
HNO <sub>3</sub>	Average Response (mV)	200	238.66	242.66	218.66	200	182.66
	$\sigma_{n-1}$	0	2.30	2.30	2.30	0	2.30
	R.S.D %	0	0.96	0.95	1.05	0	1.26
	Confidence interval of the mean $\bar{y}_i \pm t_{0.05, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	200±0	238.66±5.73	242.66±5.73	218.66±5.73	200±0	182.6±5.7
	t	420	210	192	150	156	150
	$\Delta t_B$	150	84	72	60	78	72

- **Effect of Sample Volume**

Using the optimum parameters achieved in previous section, flow rate(2.7.min<sup>-1</sup>) and potassium hexacyanoferrate(III) for the precipitation of zinc. Variable sample volumes (20, 40, 70, 80, 110  $\mu$ l) were injected through injection valve using open valve mode. Table-4 tabulates the average response of three successive measurements, standard deviation, the relative standard deviation and the confidence interval of the average response at 95% confidence.

It was noticed that any increase in the sample volume up to 100 $\mu$ l led to an increase in the height of responses followed by a constancy as shown in figure-5-A shows the plot of attenuation & reflection of incident light vs. change in sample volume( $\mu$ L).

While figure-.5-B shows a kind of response-time profile of optimum sample volumes for each acids (HClO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>). While that increase in the volume of the sample above 100 $\mu$ l leads to an increase in the response base width  $\Delta t_B$ (min) (i.e. increase analysis time). This might be attributed to the long duration of reacted sample segment, thus elute more zinc (II) ion from cationic exchange column caused sample length segment passes throughout the flow measuring cell. Therefore, 110 $\mu$ l was found to be the best sample volume for this work.



**Figure 5-** Effect of variation sample volume (µL) on, (A) Attenuation & reflection of incident light expressed as peak height (n=3) in mV, (B) Response-time profile of most optimum sample volumes for each acids (HClO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>)

**Table 4-** Effect Sample Volume upon the measurement of light attention for determination Hydronium ion.

Type of Acid	Data output	Volume of sample ( $\mu\text{L}$ )				
		20	40	70	80	110
$\text{HClO}_4$	Average Response (mV)	162.33	189.33	324	262.66	452
	$\sigma_{n-1}$	4.61	2.30	0	2.30	4
	R.S.D %	2.83	1.21	0	2.30	4
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	162.33 $\pm$ 11.4	189.33 $\pm$ 5.7	324 $\pm$ 0	262.66 $\pm$ 5.7	452 $\pm$ 9.93
$\text{H}_2\text{SO}_4$	Average Response (mV)	120	140	180	153.33	306.66
	$\sigma_{n-1}$	0	0	0	1.50	3.01
	R.S.D %	0	0	0	1.50	3.01
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	120 $\pm$ 0	140 $\pm$ 0	180 $\pm$ 0	153.3 $\pm$ 5.73	306.6 $\pm$ 22.9
$\text{HCl}$	Average Response (mV)	112	165.33	208	168	336
	$\sigma_{n-1}$	0	2.30	0	0	0
	R.S.D %	0	1.39	0	0	0
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	112 $\pm$ 0	165.33 $\pm$ 5.73	208 $\pm$ 0	168 $\pm$ 0	336 $\pm$ 0
$\text{HNO}_3$	Average Response (mV)	160	168	228	186.66	321.33
	$\sigma_{n-1}$	0	0	4	2.30	2.30
	R.S.D %	0	0	1.75	1.23	0.71
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	160 $\pm$ 0	168 $\pm$ 0	228 $\pm$ 9.9	186.66 $\pm$ 5.7	321.33 $\pm$ 5.7

- **Effect of Purge Time**

Using the optimum parameters (sample volume 110 $\mu\text{L}$ , Intensity 1.8 V, flow rate 2.7 $\text{mL}\cdot\text{min}^{-1}$  for each acids) achieved in previous sections. A study was carried out to establish the optimum allowed permissible time for the sample segment to be injected from the injection valve 2, 4,6,10,15,20,25 and 30 seconds were used for this study. Table-5 summarizes the data obtained showing the average of the three successive readings, standard deviation, relative standard deviation and the confidence interval of the average responses at 95% confidence( $\alpha=0.05$ ).

Figure-6-A show the plot of the Effect of variation for the allowed permissible time on Hydronium ion. It can be noticed from the table that there is an increase in the response with increasing the allowed permissible time for the sample injection up to 25 seconds, followed by constancy in the response. Therefore, 30 seconds was chosen as an optimum allowed permissible time for the sample segment to be injected.

For each acids ( $\text{HClO}_4, \text{HCl}, \text{HNO}_3, \text{H}_2\text{SO}_4$ ) recorded responses-time profile shown the effect of allowed permissible time upon response. When open & close injection valve for 2 second will allow sending a small amount of Hydronium ion to be carried out by the carrier stream to elute small amount of zinc (II) ion from the cation exchanger column thus, produces low response. While open & close injection valve for (4, 6, 10, 15, 20, 25 and 30sec) eluted a more of zinc (II) ion to produce high response.

Figure-6-B shows the response-time profile of results for Per chloric acid ( $\text{HClO}_4$ ) as it was obtained from Linear Array Ayah 5SX1-T-1D-CFI analyzer.

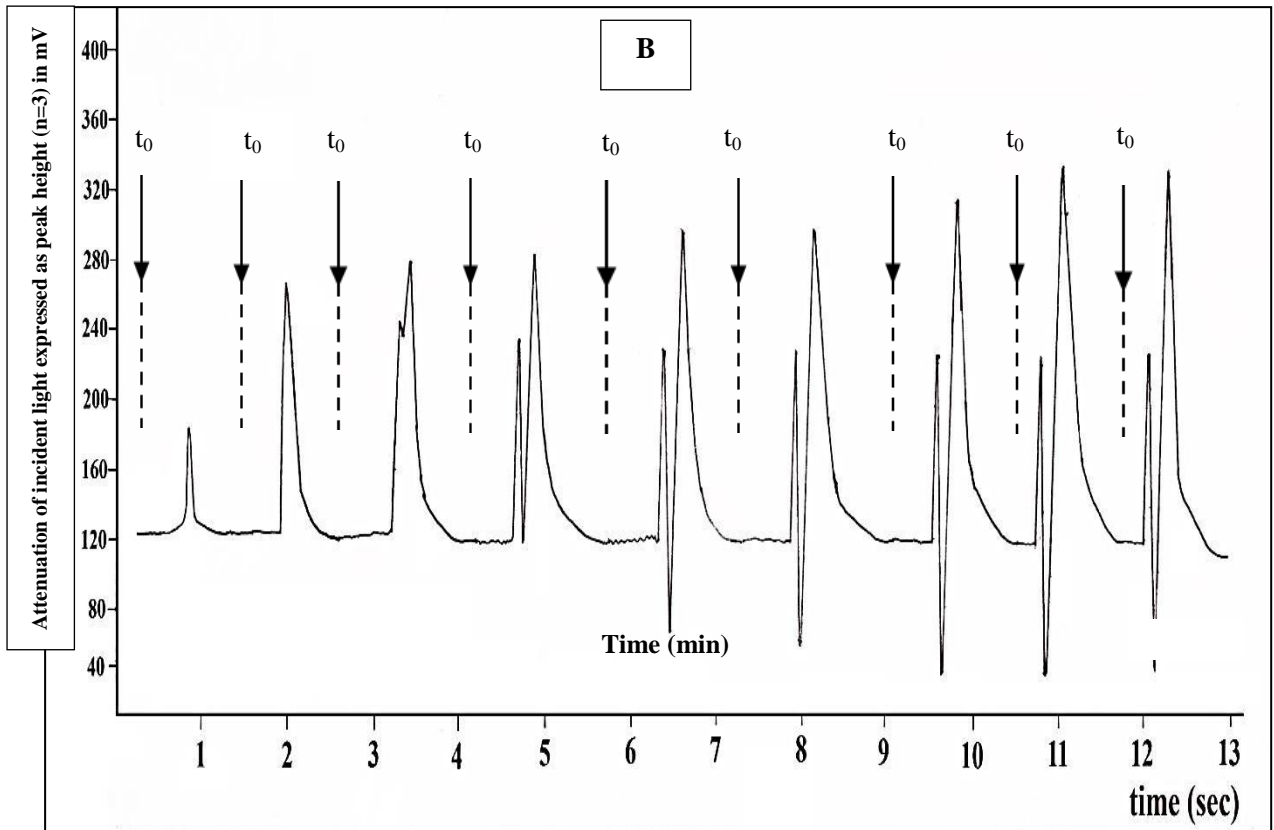
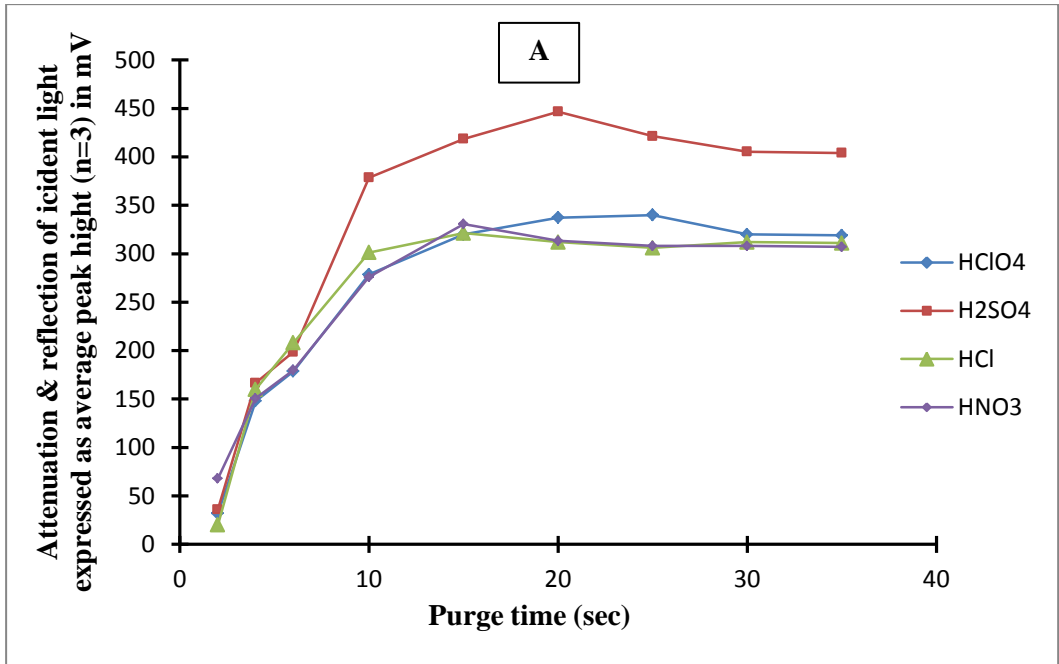


Figure 6- Effect Response-purge time variation, (A) Attenuation & reflection of incident light expressed as peak height (n=3) in mV of Hydronium ion ( $H_3O^+$ ), (B) Response profile

**Table 5-** Effect of change purge time upon the measurement of light attention for determination Hydronium ion.

Type of Acids	Data output	Purge Time ( Sec)								
		2	4	6	10	15	20	25	30	Open Valve
HClO <sub>4</sub>	Average Response (mV)	32	148	178.66	278.66	320	337.33	340	320	319
	$\sigma_{n-1}$	0	0	2.30	4.61	0	2.30	0	0	2.30
	R.S.D %	0	0	1.29	1.65	0	0.68	0	0	0.73
	Confidence interval of the mean $\bar{y}_i \pm t_{0.05, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	32±0	148±0	178.6±5.3	278.6±11.4	320±0	337.3±5.7	340±0	320±0	319±5.7 3
H <sub>2</sub> SO <sub>4</sub>	Average Response (mV)	36	166.6	198.6	378.6	418.6	446.6	421.3 3	405	404
	$\sigma_{n-1}$	0	2.30	2.30	2.30	2.30	11.547	2.30	0	4.61
	R.S.D %	1.38	1.16	0.60	0.55	2.5	0.58	0.54	0	1.139
	Confidence interval of the mean	36±0	166.6±5.7	198.6±5.7	378.6±5.7	418.6±5.7	446.6±28.6	421.33±5.73	405±0	404±11.4 4
HCl	Average Response (mV)	0	160	208	301.33	321.33	312	306.6	312	311
	$\sigma_{n-1}$	0	0	0	2.30	2.30	0	2.30	0	0
	R.S.D %	0	0	0	0.76	0.71	0	0.75	0	0
	Confidence interval of the mean	0±0	160±0	208±0	301.3±5.7	321.3±5.7	312±0	306.6±5.7	312±0	311±0
HNO <sub>3</sub>	Average Response (mV)	68	150.66	180	276	330.33	313.33	308	308	307
	$\sigma_{n-1}$	0	2.30	4	0	4.6	2.30	0	0	0
	R.S.D %	0	1.53	2.2	0	1.39	0.737	0	0	0
	Confidence interval of the mean	68±0	150.6±5.7	180±9.9	276±0	330.3±11.4	313.3±5.7	308±0	308±0	307±0

### 3.2 Calibration graph

The results for variation of Hydronium ion concentration was obtained under the optimized conditions (for each acids). A series of variable concentration ranging from 0.01 to 0.1 mol.L<sup>-1</sup> were prepared for the purpose of using them for the preparation of scatter plot diagram followed by the choice of calibration graph. The obtained results were tabulated in table -6 while their representation was in figure-7 which shows the variation of response with concentration of Hydronium ion.

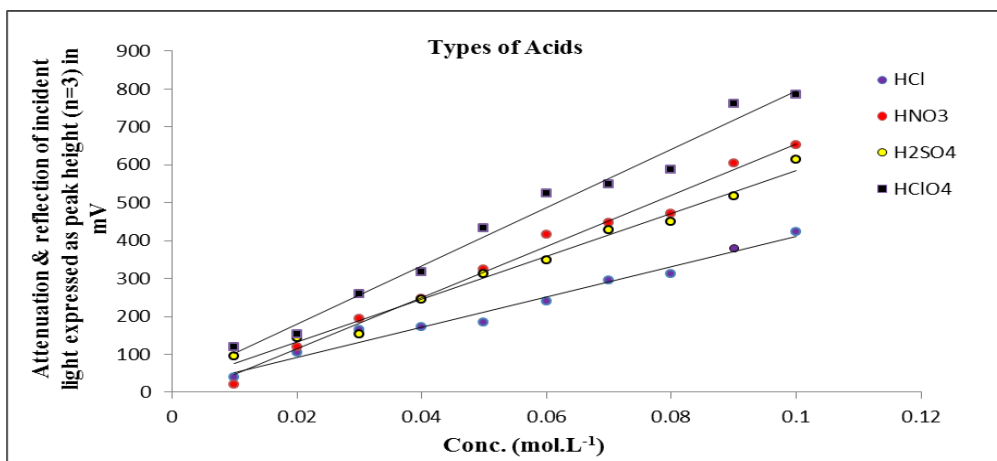


Figure 7- Calibration graph for Hydronium ion Conc (mol.L<sup>-1</sup>) for each acids acids (HClO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>)

Table 6- Summary of calibration graph result of Hydronium ion for each acids

Type of acids	Concentration range (mol.L <sup>-1</sup> )	$\bar{Y}(mV)=a\pm S_a t+b\pm S_b t[X]$ at confidence interval 95%	$r_2$ $r^2\%$	$t_{tab}$ at 95%	Calculated t- value $= \frac{ r \sqrt{n-2}}{\sqrt{1-r^2}}$
HClO <sub>4</sub>	0.01-0.1	$26.48\pm 49.15+7673.53\pm 792.37[X]$	0.9891 0.7985 97.85%	2.262	21.90
H <sub>2</sub> SO <sub>4</sub>	0.01-0.1	$18.93\pm 33.29+5663.03\pm 536.84[X]$	0.9930 0.9861 98.61%		23.86
HCl	0.01-0.1	$13.06\pm 29.1798+3973.33\pm 208.04[X]$	0.9917 0.9836 98.36%		19.09
HNO <sub>3</sub>	0.01-0.1	$21.95\pm 36.73+6760.40\pm 592.07[X]$	0.9940 0.9881 98.81%		25.82

[X] concentration of Hydronium ion (mol.L<sup>-1</sup>)

### 3.3 Limit of Detection (L.O.D)

A study was carried out to determine the limit of detection of Hydronium ion via successive gradual dilution of the minimum concentration in the linear range which. Table-7 shows the limit of detection conducted by three different methods taking into account the dilution factor and the path length of the flow cell used.

Table 7- limit detection of Hydronium ion at optimum parameters for each acids

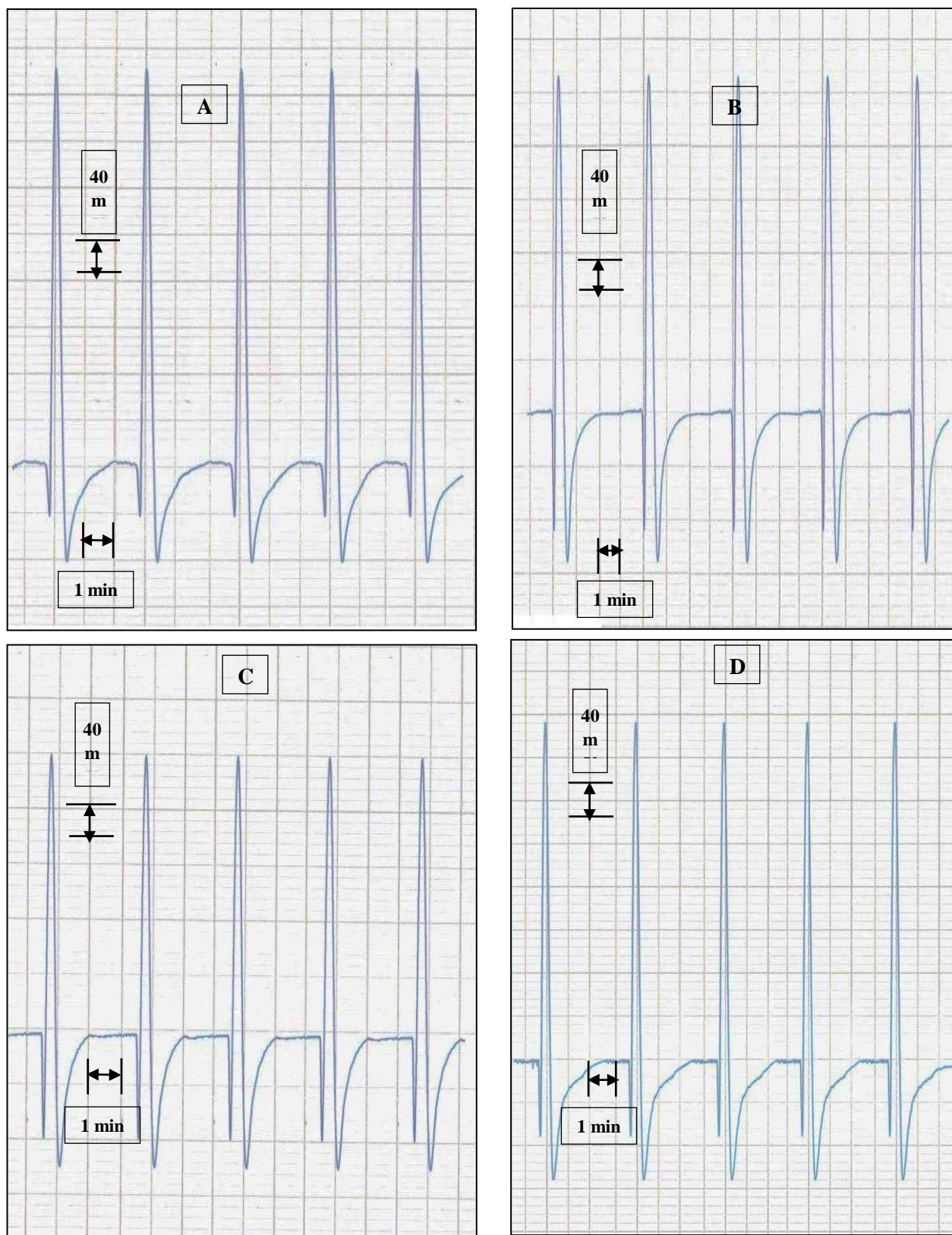
Type of acids	Minimum concentration (mM)	Practical based on gradual dilution of minimum concentration	Theoretical based on the value of slope $X=3S_B/\text{slope}$	Theoretical based on the linear equation $\hat{Y}=Y_B+3S_B$
HClO <sub>4</sub>	3	30 $\mu\text{g/sample}$	40.06 $\text{ng/sample}$	127.466 $\mu\text{g/sample}$
H <sub>2</sub> SO <sub>4</sub>	5	50.01 $\mu\text{g/sample}$	52.98 $\text{ng/sample}$	114.22 $\mu\text{g/sample}$
HCl	8	29.75 $\mu\text{g/sample}$	28.07 $\text{ng/sample}$	53.05 $\mu\text{g/sample}$
HNO <sub>3</sub>	8	51.41 $\mu\text{g/sample}$	28.520 $\text{ng/sample}$	67.80 $\mu\text{g/sample}$

### 3.4 The Repeatability of Hydronium ion

The repeatability of measurements and the efficiency of homemade 5Sx1-1D-solar FI microphotometer[18] were studied at fixed concentrations Hydronium ion (for each acids) (mainly two concentrations were used. 0.02, 0.08 M) using the optimum parameters(sample volume 110 $\mu$ l, Intensity 1.8 V, flow rate 2.7mL.min<sup>-1</sup> for each acids). A repeated measurements for five successive injections were measured and the obtained results is tabulated in table-8 which shows that the percentage relative standard deviation was less than 2%, while figure-8-A,B,C,D shows a kinds of response-time profile for the used concentrations

**Table 8-** Repeatability of Hydronium ion for each acids result

Type of Acids	Data output	Hydronium ion (mol.L <sup>-1</sup> )	
		0.02	0.08
HClO <sub>4</sub>	Average Response (mV)	154	589
	$\sigma_{n-1}$	1	1
	R.S.D %	0.64	0.16
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	154 $\pm$ 2.48	589 $\pm$ 2.48
H <sub>2</sub> SO <sub>4</sub>	Average Response (mV)	144	449.33
	$\sigma_{n-1}$	1	2.30
	R.S.D %	0.68	0.51
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	144 $\pm$ 2.48	449.33 $\pm$ 5.73
HCl	Average Response (mV)	104	312
	$\sigma_{n-1}$	0.76	1
	R.S.D %	0.72	1
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	104 $\pm$ 1.89	312 $\pm$ 2.48
HNO <sub>3</sub>	Average Response (mV)	121	473
	$\sigma_{n-1}$	1	1.73
	R.S.D %	0.84	0.36
	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2}, n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$	121 $\pm$ 2.48	473 $\pm$ 4.303



**Figure 8-** Five successive repeatable measurement ( $80 \text{ mMol.L}^{-1}$ )  $110 \mu\text{L}$ , flow rate ( $2.7 \text{ mL.min}^{-1}$ ) of  
A- HClO<sub>4</sub>  
B- HCl  
C- H<sub>2</sub>SO<sub>4</sub>  
D- HNO<sub>3</sub>



### 3.5 Classical method:-

Calibration graph of classical method measurement of Hydronium ion by a calibrated PH meter was achieved for determination of Hydronium ion in the range 0.01-0.1 mol.L<sup>-1</sup> for used acid. Table-9 tabulates all obtained data. table-10 summarizes paired t-test between the newly developed method and PH meter; it shows that there were no significant differences between either methods. i.e.; the new developed method can be used as an alternative method for measurement of acidity based on the reaction sequence mentioned in this work.

**Table 9-** Summary of PH meter measurements for each acids

Type of acids	Concentration range (mol.L <sup>-1</sup> )	$\bar{Y}(mV)=a\pm S_a t+b\pm S_b t[X]$ at confidence interval 95%	$r$ $r^2$ $r^2\%$	$t_{tab}$ at 95% Confidence interval	Calculated t- value $= \frac{ r \sqrt{n-2}}{\sqrt{1-r^2}}$
HClO <sub>4</sub>	0.01-0.1	234.21±0.884+321.75±14.25[X]	0.9984 0.9969 99.69%	2.262	51.033
H <sub>2</sub> SO <sub>4</sub>	0.01-0.1	227.61±1.47+275.93±23.66[X]	0.9942 0.9942 99.42%		26.28
HCl	0.01-0.1	229.52±3.95+350.06±64.08[X]	0.9747 0.9501 95.01%		12.35
HNO <sub>3</sub>	0.01-0.1	227.16±6.51+490.60±105.02[X]	0.9659 0.9331 93.31%		10.56

[X] concentration of Hydronium ion (mol.L<sup>-1</sup>)

**Table 10-** Paired t-test

Type of acids	Comparison between flow injection & classical methods (mol.L <sup>-1</sup> )		Paired Differences			t Cal. $t = \frac{\bar{X}_d \sqrt{n}}{\sigma_{n-1}}$	df	Sig. (2-tailed) at 95% Confidence interval	t critical at 95% Confidence interval	t critical at 99% confidence interval
	Flow method	Classical method	Mean	Std. Deviation	Std. Error Mean					
HClO <sub>4</sub>	0.01-0.1	0.01-0.1	357.2	224.57	71.0165	2.76	9	0.022	2.262	3.250
H <sub>2</sub> SO <sub>4</sub>	0.01-0.1	0.01-0.1	217.8	170.56	53.9366	1.77	9	0.109		3.250
HCl	0.01-0.1	0.01-0.1	62.40	111.25	35.1814	0.48	9	0.637		3.250
HNO <sub>3</sub>	0.01-0.1	0.01-0.1	232.3	191.037	60.4113	1.58	9	0.148		3.250

### Application:-

Two methods used for determination Hydronium ion HCl (36.5-38.0%, country: U.S.A) in commercial samples. The methods were used firstly method was Linear Array Ayah 5SX1-T-1D-Continuous flow injection analyzer[18].while the second method was PH meter. A series of variable concentration ranging from 0.05 to 0.08 mol.L<sup>-1</sup> were prepared for this purpose.

Using paired t-test between the newly developed method and classical method; shows no significant differences between either methods. Table-11 summarizes paired t-test between newly method and PH meter; in commercial samples.

**Table 11-** Paired t-test for samples

Type of acids	Comparison between flow injection & classical methods (mol.L <sup>-1</sup> )	Paired Differences					t Cal. $t = \frac{\bar{X}_d \sqrt{n}}{\sigma_{n-1}}$	df	Sig. (2-tailed)	critical at 95% confidence interval
		Mean $\bar{X}_d$	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference					
					lower	upper				
HCl	0.05-0.08	22.90	72.212	37.606	96.77	142.57	0.609	3	0.586	3.182

### Conclusion

The proposed turbidmetric flow-injection method is simple, rapid, inexpensive and sensitive for the determination of Hydronium ion. The method based on reaction between eluted Zinc (II) by Hydronium ion from cation exchange column with potassium hexacyanoferrate (III) to form pale yellow precipitate as ion pair complex. The new method can be used to determine of Hydronium ion in pure and commercial samples without needing for calibrated, solution buffer and electrodes. The precipitate is measured via the attenuation of incident light by Linear Array Ayah 5SX1-T-1D-Continuous flow injection analyzer[18]. The %R.S.D was < 2% and good agreements were observed for all samples, which is an indication of satisfactory accuracy of the proposed method. A final conclusion can draw that at  $\alpha=0.05$  (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl) used in this work will be accepted to be determination by the developed method. While at  $\alpha=0.01$  all acids can be determined.

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