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Research Article

NOVEL METHOD FOR DETERMINATION OF HYDROCHLORIC ACID VIA ION EXCHANGE AND PRECIPITATION REACTION INDIRECTLY BY USING LINEAR ARRAY AYAH 5SX1-T-1D CONTINUOUS FLOW INJECTION ANALYSER

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ABSTRACT

A new Turbidimetric method characterized by simplicity, accuracy and speed for determination of Hydronium ionby continuous flow injection analysis. The method was based on the formation of complex $Cu_3[Fe(CN)_6]$ for Copper (II) that was eluted by Hydronium ion from cation exchanger column with Potassium hexacyanoferrate(III) for the formation of a green dark precipitate and this precipitate was determined using homemade Linear ArrayAyah-5SX1-T-1D continuous flow injection analyser. The optimum parameters were 3.1 $mL.min^{-1}$ flow rate using H_2O as a carrier stream, 2 $mL.min^{-1}$ reagent stream, 110 μL sample volume and open valve for the purge of the sample segment. Data treatment shows that linear range 0.01-0.1 $mol.L^{-1}$for Hydrochloric acid while L.O.D 4.01 μg/sample for HCl from the stepwise dilution for minimum concentration of lowest concentration in linear dynamic range of the calibration graph. The correlation coefficient (r) was 0.9863 while percentage linearity ($\%r^2$) was 97.28% for HCl . R.S.D. % for the repeatability (n=5) was < 2% for determination of Hydrochloric acid with concentration 20 and 100 $mMol.L^{-1}$. 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.

INTRODUCTION

Acids are essential substances in home, industry, and the environment. In aqueous solution, water combines with the proton released from an acid to from the hydrated species represented by H_3O^+ (aq). In the Arrhenius definition, acids contain H^+ and yield H_3O^+ in water. Acid strength depends on $[H_3O^+]$ relative to [HA] in aqueous solution[1]. A Lewis acid is a substance that can accept a pair of electrons to form a covalent bond. Examples of Lewis acids include all metal cations, and electron-deficient molecules such as boron trifluoride and aluminiumtrichloride.

Hydrochloric acid is a clear, colorless, highly pungent solution of hydrogen chloride (HCl) in water. It is a highly corrosive, strong mineral acid with many industrial uses. Hydrochloric acid is found naturally in gastric acid. Historically called acidumsalis, muriatic acid, and spirits of salt, hydrochloric acid was produced from vitriol (sulfuric acid) and common salt. With major production starting in the Industrial Revolution, hydrochloric acid is used in the chemical industry as a chemical reagent in the large-scale production of vinyl chloride for PVC plastic, and MDI/TDI for polyurethane. It has numerous smaller-scale applications, including household cleaning, production of gelatin and other food additives, descaling, and leather processing. About 20 million tonnes of hydrochloric acid are produced worldwide annually[2-8].This work, describes a simple turbidmetric flow injection method that have been developed for the determination of Hydronium ion. The method is based on the reaction between eluted Copper by Hydronium ion from cation exchange column packed with potassium hexacyano ferrate (III) $K_3[Fe(CN)_6]$ to form green dark 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 copper nitrate Cu $(NO_3)_2.3H_2O$. (BDH, 0.3 $mol.L^{-1}$) was prepared by dissolving 7.248 g in 100 mL distilled water. A stock solution of potassium hexacyanoferrate (III) $K_3[Fe(CN)_6]$ was prepared by dissolving 32.926 g in 500 mL of distilled water. Hydrochloric Acid solution (38%, 1.19 $g.mL^{-1}$, BDH, 2 $mole.L^{-1}$) was prepared by pipetting 323 mL of concentrated Hydrochloric acid and complete the volume with distilled water to 2000 mL of volumetric flask. The acid was standardized against Sodium Carbonate Na_2CO_3 Solution (BDH, 2 $mol.L^{-1}$).

2.2 Preparation of column

Few grams of strong cation exchange resin (amberlite 120- Na^+) was taken and washed with distillated 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 H^+ form; followed by constant wash with distillated 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 in this form is ready for use.

2.3 Preparation of the resin for determination of acid

A saturated solution of Copper nitrate 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 copperion(II). This process should be continuous until there is a positive test that copper 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 copper 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[9] 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.

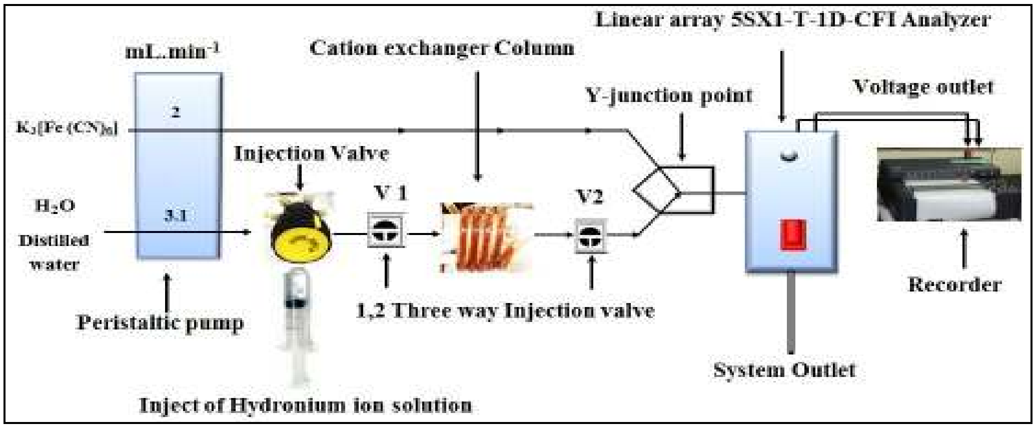
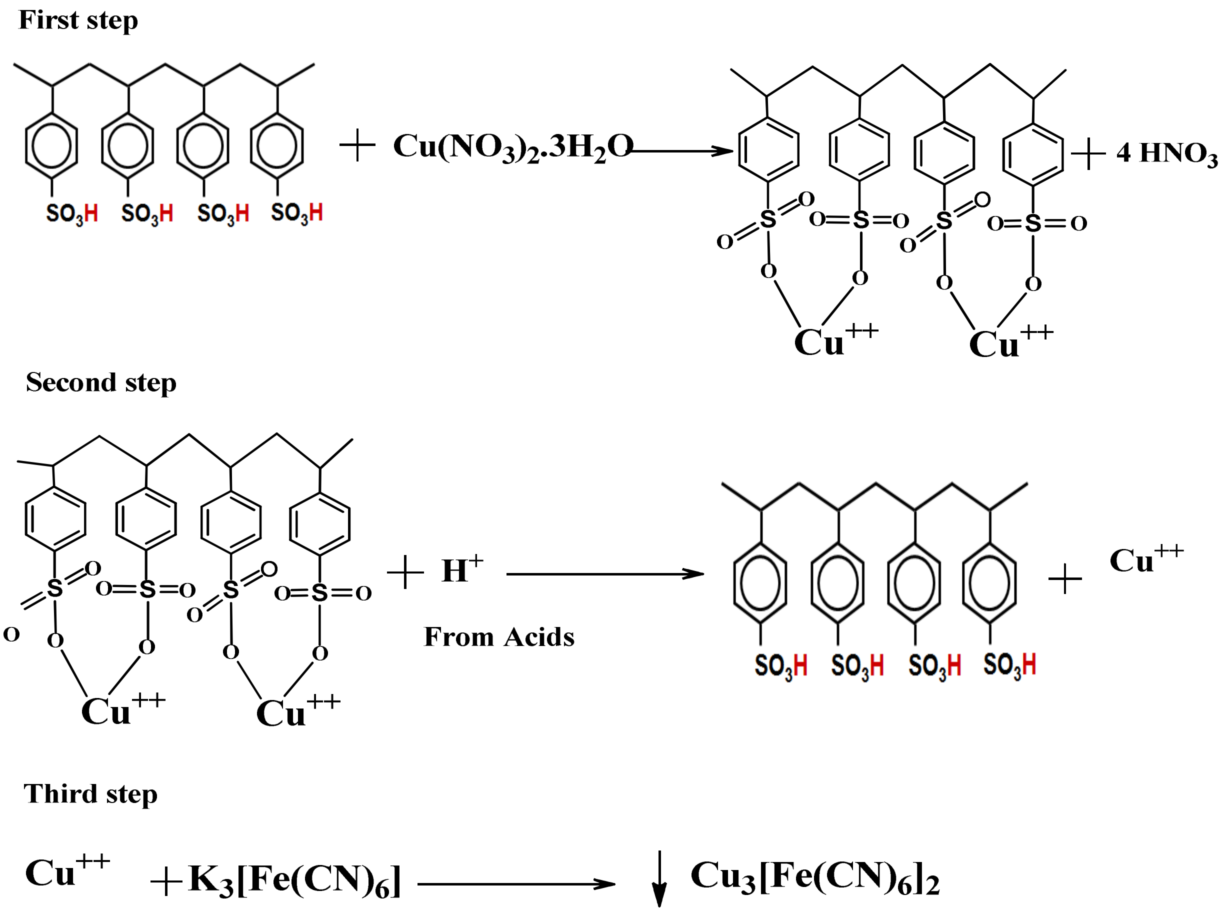


Fig. 1: Schematic diagram of flow injection analysis system used for determination of Hydronium ion, V_1 and V_2 three way injection valves

2.5 Methodology

The flow diagram shown in fig.1, for determination of Hydrochloric acid, by the reaction between potassium hexacyanoferrate(III) and Copper (II) ion that eluted from cation exchange Column by Hydronium ion to form dark green precipitate from complex $Cu_3[Fe(CN)_6]_2$ which is composed of two lines : the first line is the carrier stream (distilled water) at 3.1 ml.min^{-1} flow rate which passes to injection valve to carry Hydronium ion sample (110 µL) then passes through cation exchange Colum to elute the copper; while the second line is the reagent stream supplies $K_3[Fe(CN)_6]$ solution 0.03(mol.L^{-1}) at 2 mL.min^{-1}. Both line meet at a junction (Y-junction), with an outlet for reactants product from $Cu_3[Fe(CN)_6]_2$ 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 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 attenuation light that collides on the surfaces of precipitated particles 0-180°. A proposed mechanism of charging the resin with Cu (II) ion followed by elution show in scheme 1.



Scheme 1: Proposed mechanism for $Cu_3[Fe(CN)_6]_2$ complex formation

3. RESULTS AND DISCUSSION

3.1 Study of the optimum parameters :-

The flow gram shown in show fig.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 varing one at each time.

3.1.1 Chemical Variables

3.1.1.1 Effect of $K_3[Fe(CN)_6]$ Concentration:-

Using the preliminary experimented parameters of Hydronium ion 0.05 mol.L^{-1}, intensity of incident light of LED$_s$1.8 V, flow rate of carrier stream and reagent stream 2.7ml.min^{-1} and 1.7 ml.min^{-1} respectively at 80μl 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 hexacyanoferrate(III) in the range of 0.01 to 0.1 mole.L^{-1} for Hydrochloric acid that can be used for formation a green dark precipitate of $Cu_3[Fe(CN)_6]_2$ by eluted Copper (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(α=0.05). Fig.2 (A) show Effect of potassium hexacyano ferrate (III) $K_3[Fe(CN)_6]$ 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 hexacyanoferrate (III) concentration was 0.03 mol.L^{-1}for HCl. 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 hexacyanoferrate (III) concentration Higher than 0.03 mol.L^{-1} for HCl leads to a significant differences in the response. This might be due to increase in amount of precipitate, thus leading to a decrease in attenuation of light; this causes a decrease in peak height resulting from measurement. Therefore, 0.03 mol.L^{-1} for (HCl)was chosen as an optimum concentration for the precipitation. Fig.2 (B) shows the response-time profile of the optimum results acids (HCl) as it was obtained from Linear Array Ayah 5SX1-T-1D-CFI analyzer.

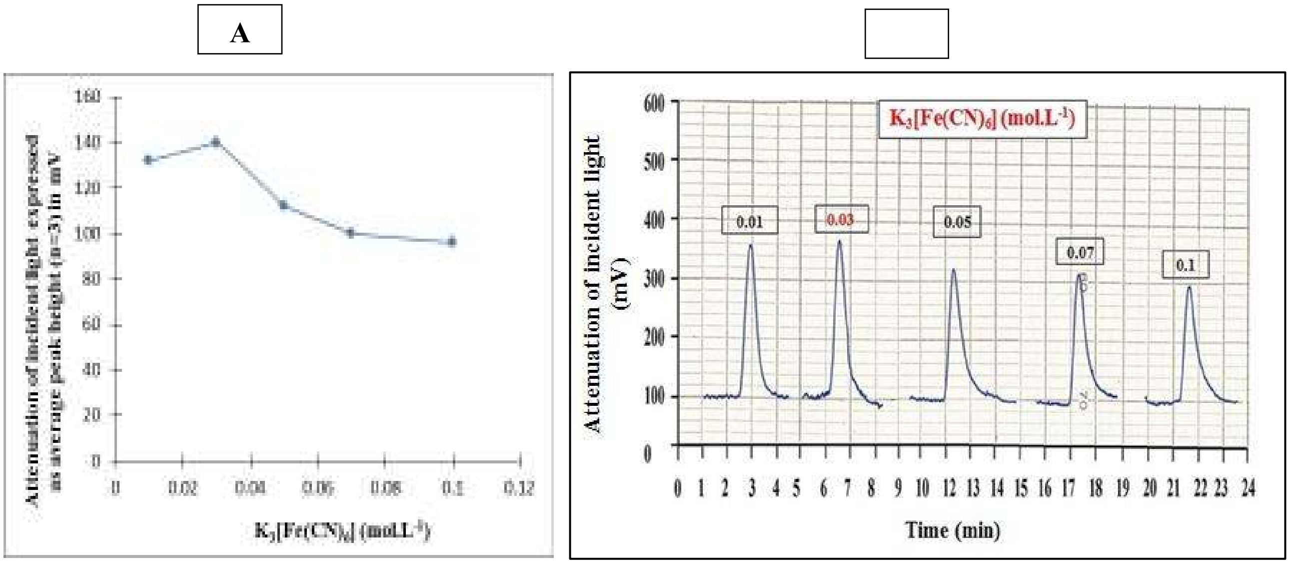


Fig. 2: Effect of hexacyano ferrate (III) $K_3[Fe(CN)_6]$ concentration (mol.L^{-1}) on (A): Attenuation of incident light (mV) for Hydrochloric acid (0.1 mol.L^{-1}) 80μL, flow rate of carrier stream and reagent stream 2.7 and 1.7 ml.min^{-1} respectively. (B): Response profile

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

Type of acids	Conc.of $K_3[Fe(CN)_6]$ (Mol.L^{-1})	Average Response $\bar{y}_i$ (mV)	σ_{n-1}	R.S.D %	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2},n-1}\frac{\sigma_{n-1}}{\sqrt{n}}$
HCl	0.01	132	0	0	132±0
	0.03	140	0	0	140±0
	0.05	113.33	1.15	1.018	113.33±8.60
	0.07	100	0	0	100±0
	0.1	96	0	0	96±0

3.1.2 Physical Variables

3.1.2.1 Variation of Incident Light Intensity

A variable intensity of white LEDs light source (0.2-2) V was used for this study, and the system used for determination of Hydrochloric acid (0.05 mol.L^{-1} for all physical parameters) via formation of a dark green precipitate, 80 µL sample volume and optimum concentration of $K_3[Fe(CN)_6]$ (0.03) mol.L^{-1} for HCl. 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(α=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 Hydrochloric acid. Fig.3 (A)shows the plot of attenuation of incident light vs. change in intensity of incident light.Fig.3 (B) shows the response-time profile as it was obtained from Linear Array Ayah 5SX1-T-1D-CFIanalyser.

3.1.2.2 Effect of Flow Rate

A set of experiments were conducted for the optimization of the preferred flow rate (0.9-3.7ml.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 Δt_B(sec).

It was noticed from the results obtained that there were no significant differences in the response height at low flow rate(<1.8ml.min^{-1}) even the response show a wider base width (increase analysis time) as shown in fig.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 2.7ml.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 Copper ion (II) 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 2.7ml.min^{-1} and 1.7 ml.min^{-1} of reagent stream were chosen as optimum flow rate throughout this work. Fig.4 (B) shows the response-time profile of results for acids (HCl) as it was obtained from Linear Array Ayah 5SX1-T-1D-CFIanalyzer. .

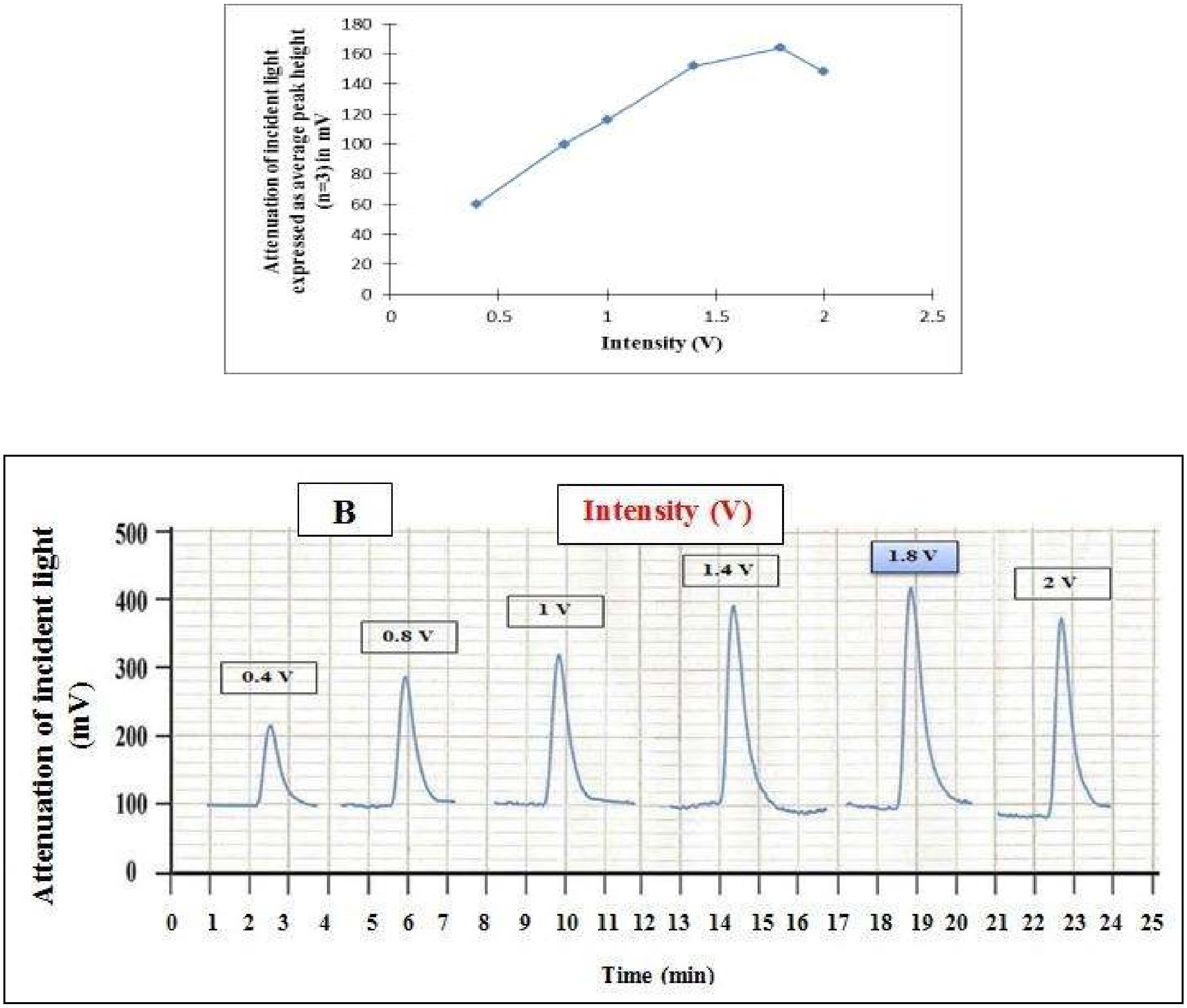


Figure 3: Effect of attenuation of incident light (mV) on
(A): Variation of intensity expressed in V.
(B): shows the response-time profile

Table 2: Effect of intensity on attenuation of incident light for determination Hydrochloric acid

Type of acids	Intensity (V)	Average Response $\bar{y}_i$ (mV)	σ_{n-1}	R.S.D %	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2},n-1}\frac{\sigma_{n-1}}{\sqrt{n}}$
HCl	0.4	60	0	0	60±0
	0.8	100	0	0	100±0
	1	116	0	0	116±0
	1.4	152	0	0	152±0
	1.8	164	0	0	164±0
	2	148	0	0	148±0

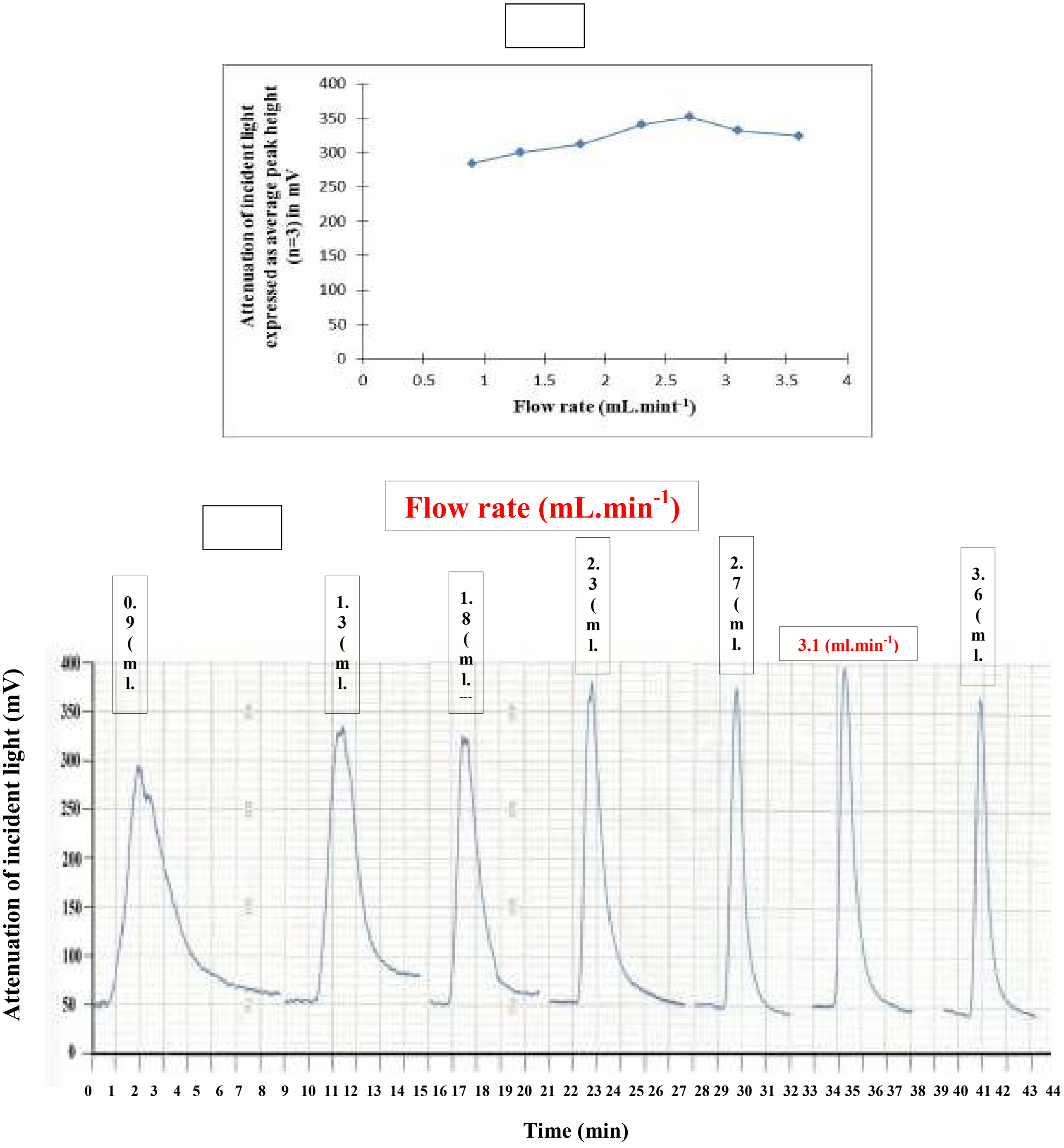


Figure 4: Effect of variation of flow rate (ml.min^{-1}) on
(A) Attenuation of incident light expressed as peak height (n=3) in mV
(B) Response profile.

Table 3: Effect of flow rate on attenuation of incident light for determination Hydrochloric acid

Type of acids	Flow Rate (mL.mint^{-1})	Average Response $\bar{y}_i$ (mV)	σ_{n-1}	R.S.D %	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2},n-1}\frac{\sigma_{n-1}}{\sqrt{n}}$	Base width Δt_B (sec)	t (sec)
HCl	0.9	285.33	2.30	0.80	285.33±5.73	360	660
	1.3	301.33	2.30	0.76	301.33±5.73	240	420
	1.8	312	0	0	312±5.73	210	360
	2.3	341.33	2.30	0.67	341.33±5.73	180	300
	2.7	352	0	0	352±5.73	120	270
	3.1	333.33	2.30	0.69	333.33±5.73	120	240
	3.6	324	0	0	324±0	90	210

3.1.2.3 Effect of Sample Volume

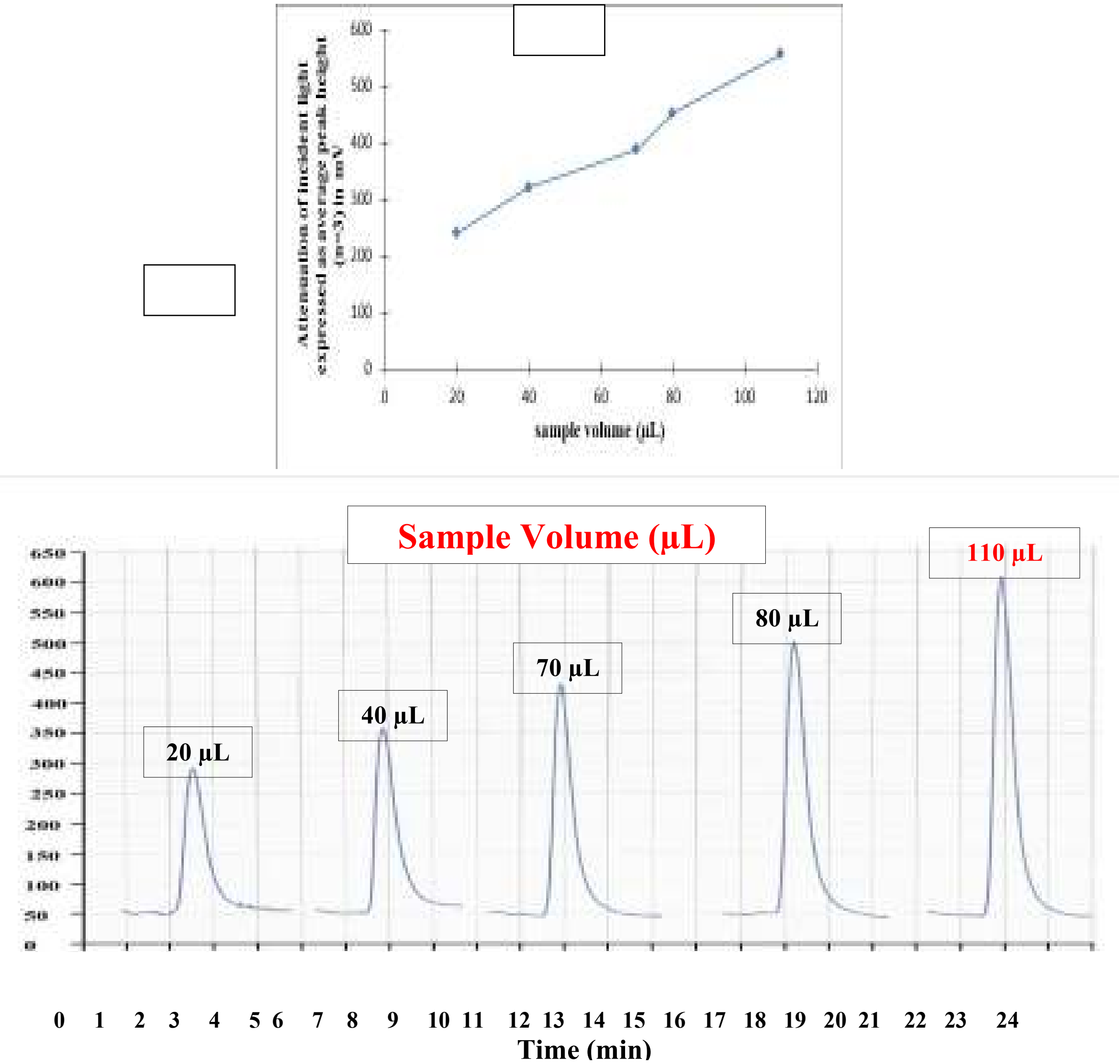
Using the optimum parameters achieved in previous section, flow rate(3.1.min^{-1}) and potassium hexacyanoferrate(III) for the precipitation of Copper (II) ion. Variable sample volumes (20, 40, 70, 80, 110 µl) were injected through injection valve using open valve mode. Table (4) tabulates the average 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 100µl led to an increase in the height of responses followed by a constancy as shown in fig.5 (A) shows the plot of attenuation of incident light vs. change in sample volume(µL).While fig.5 (B) shows a response-time profile of optimum sample volume for each acid (HCl). While that increase in the volume of the sample above 100µl leads to an increase in the response base width Δt_B(min) (i.e. increase analysis time). This might be attributed to the long duration of reacted sample segment, thus elute more Copper ion (II) ion from cationic exchange column caused sample length segment passes throughout the flow measuring cell. Therefore, 110µl was found to be the best sample volume for this work.

3.1.2.4 Effect of Purge Time

Using the optimum parameters (sample volume 110µl, Intensity 1.8 V, flow rate 3.1 mL.min^{-1} 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(α=0.05).

Fig.6 show the plot of the Effect of variation for the allowed permissible time on Hydrochloric acid. 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, 35 seconds was chosen as an optimum allowed permissible time for the sample segment to be injected.



(A) Attenuation of incident light (mV)

(B) Response-time profile of sample volumes for Hydrochloric acid

Table 4: Effect of Sample Volume onattenuation of incident light fordetermination Hydrochloric acid

Type of acids	Sample volume (µL)	Average Response $\bar{y}_i$ (mV)	σ_{n-1}	R.S.D %	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2},n-1} \frac{\sigma_{n-1}}{\sqrt{n}}$
HCl	20	241.33	2.30	0.95	241.33±5.73
	40	321.33	2.30	0.71	321.33±5.73
	70	389.33	2.30	0.59	389.33±5.73
	80	452	0	0	452±0
	110	556	0	0	556±0

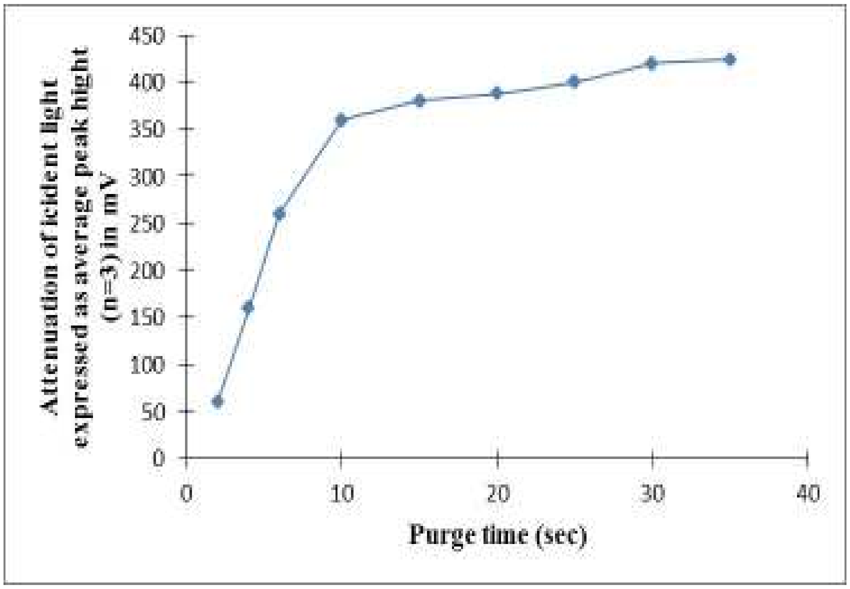


Fig. 6: Variation of purge time onattenuation of incident light expressed as peak height (n=3) in mV of Hydrochloric acid

Table 5: Effectof purge time on attention of incident light for determination Hydrochloric acid

Type of acids	Purge time (Sec)	Average Response $\bar{y}_i$ (mV)	σ_{n-1}	R.S.D %	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2},n-1}\frac{\sigma_{n-1}}{\sqrt{n}}$
HCl	2	60	0	0	60±0
	4	160	0	0	160±0
	6	260	2.30	0.89	260±5.73
	10	360	2.30	0.63	360±5.73
	15	380	0	0	380±0
	20	388	2.30	0.59	388±5.73
	25	400	2.30	0.57	400±5.73
	30	420	0	0	420±0
	35	424	0	0	424±0
	Open valve	426	0	0	426±0

3.2 Calibration graph

The results for variation of Hydrochloric acid concentration was obtained under the optimized conditions. A series of variable concentration ranging from 0.01 to 0.1 mol.L^{-1} 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 Fig.7 which shows the variation of response with concentration of Hydrochloric acid.

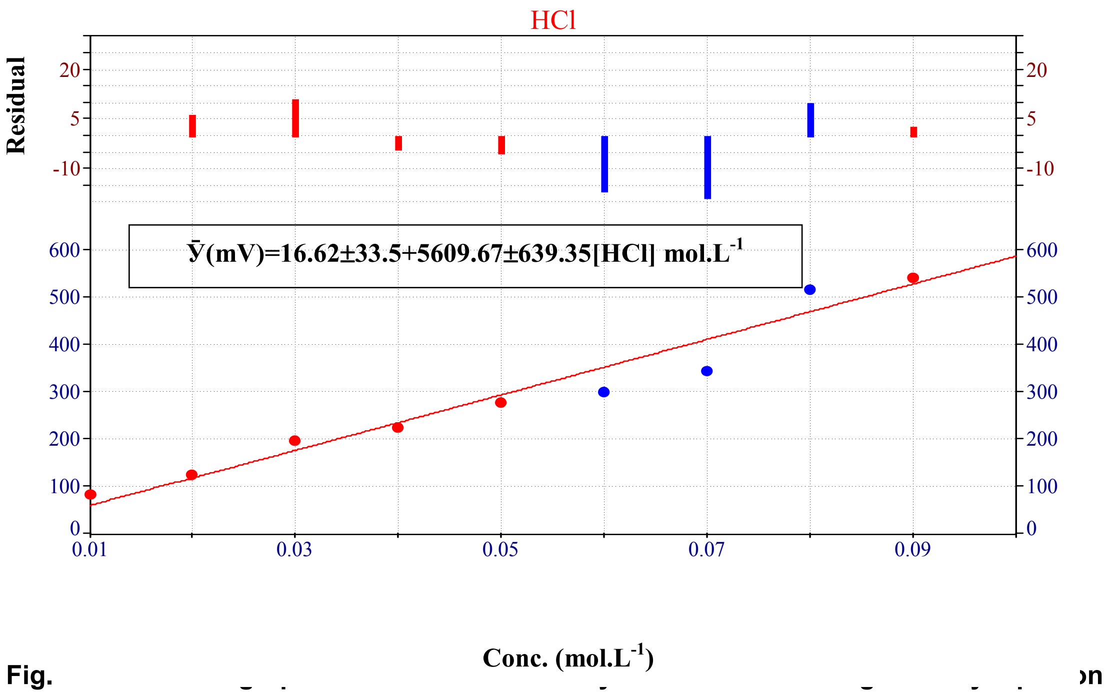


Fig. on

Table 6: Summary results of calibration graph result for Hydrochloric acid using Cu(++) loaded on cationexchanger column

Concentration range (mol.L^{-1})	Ȳ(mV)=a±S$_a$t+b±S$_b$t[X] at confidence interval 95%	r r^2 r^2%	t$_{tab}$ at 95%	Calculated t-value $=\frac{\lvert r\rvert\sqrt{n-2}}{\sqrt{1-r^2}}$
0.01-0.1	16.62±33.5+5609.67±639.35[X]	0.9863 0.9728 97.28%	2.262	19.84

[X] concentration of Hydrochloric acid (mol.L^{-1})

3.3 Limit of Detection (L.O.D)

A study was carried out to determine the limit of detection of Hydrochloric acid 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 of detection for Hydrochloric acid at optimum parameters using (110µL)

Type of acids	Minimum concentration (mM)	Practical based on gradual dilution of minimum concentration	Theoretical based on the value of slope X=3S$_B$/slope	Theoretical based on the linear equation $\hat{Y}=Y_B+3S_B$
HCl	1	4.01 µg	21.44 ng	72.04 µg

3.4 The Repeatability of Hydronium ion

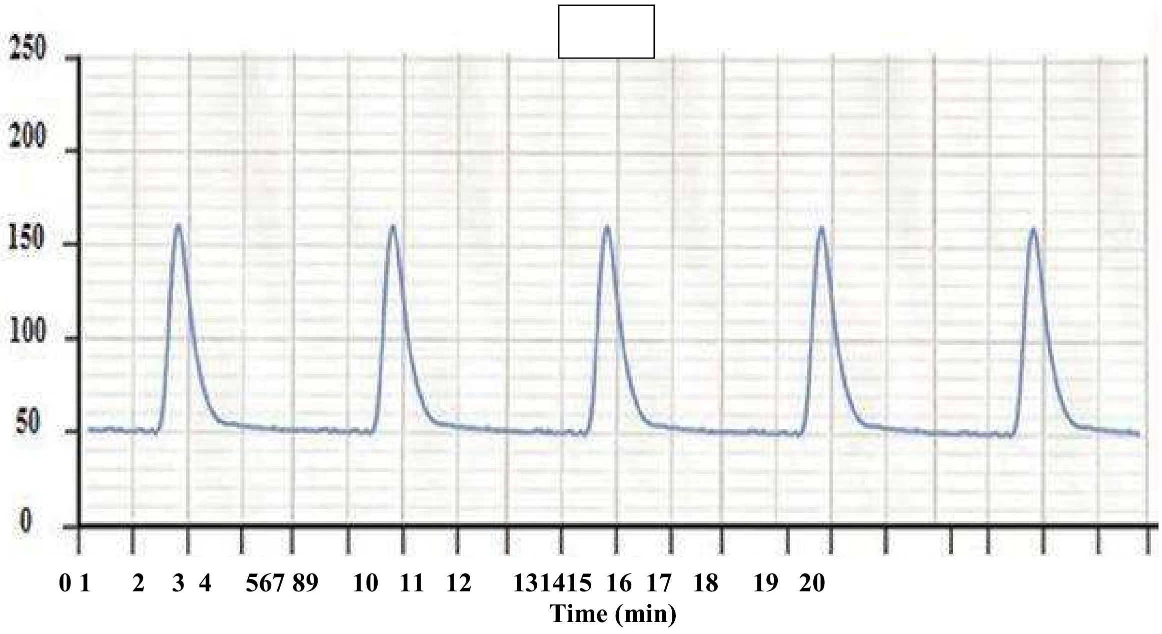
The repeatability of measurements and the efficiency of homemade 5Sx1-1D-solar FI microphotometer[9]were studied at fixed concentrations Hydronium ion mainly two concentrations were used (0.03, 0.1 M) using the optimum parameters(sample volume 110µl, Intensity 1.8 V, flow rate 3.1 mL.min^{-1}. A repeated 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,) shows a kinds of response-time profile for the used concentrations.

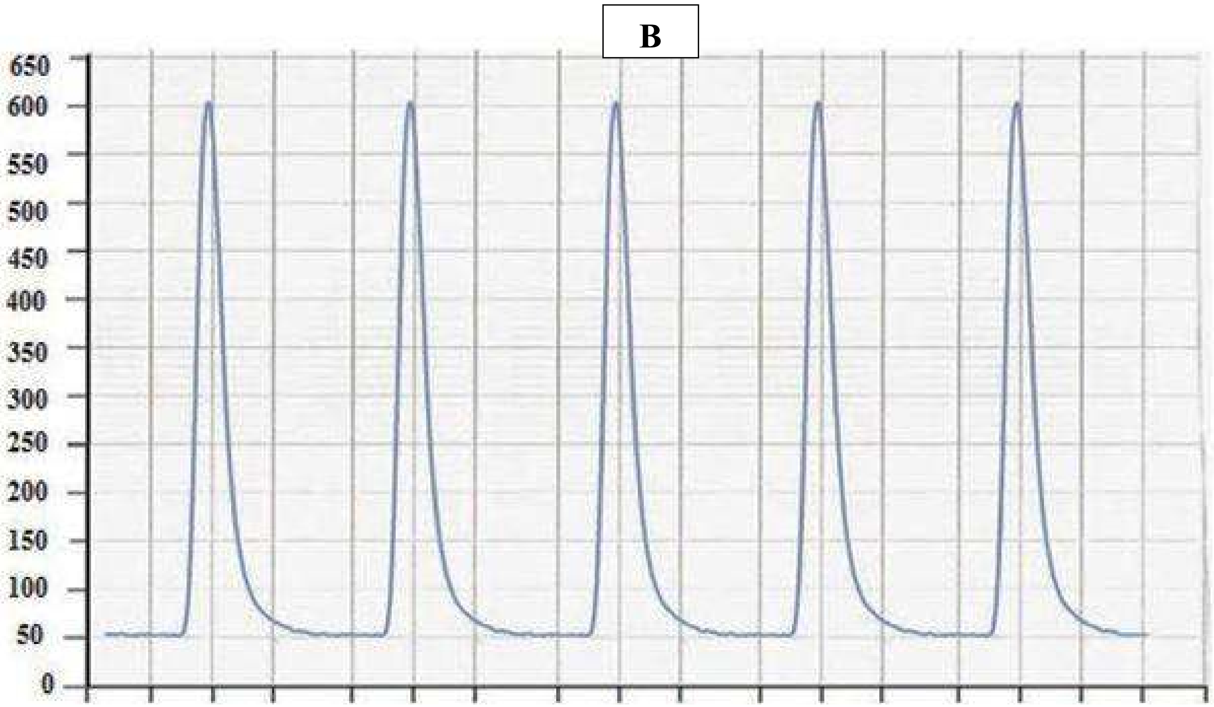
3.5 Classical method:-

Calibration graph of classical method measurement of Hydrochloric acid by a calibrated PH meter was achieved in the range 0.01-0.1 mol.L^{-1}. Table (9) tabulates all obtained data. While 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 8: Repeatability of Hydrochloric acid

Concentration (mol.L^{-1})	Average Response $\bar{y}_i$ (mV)	σ_{n-1}	R.S.D %	Confidence interval of the mean $\bar{y}_i \pm t_{\frac{0.05}{2},n-1}\frac{\sigma_{n-1}}{\sqrt{n}}$
0.02	125.33	2.30	1.84	285.33±5.73
0.1	301.33	2.30	0.65	301.33±5.73





(20 mMol.L^{-1}and 100 mMol.L^{-1}) 110µL, flow rate (3.1 mL.min^{-1})

Table 9: Summary of PH meter measurements Hydrochloric acid

Comparison between flow injection & classical methods (mol.L^{-1})		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
Linear array Ayah 5SX1-T-1D C.F.I	PH meter	Mean $\bar{x}_d$	Std. Deviation					
0.01-0.1	0.01-0.1	72.82	169.919	1.355	9	0.208	2.262	3.250

[X] concentration of Hydronium ion (mol.L^{-1})

Table 10: Paired t-test for standard solution

Concentration range (mol.L^{-1})	$\bar{y}$(mV)=a±S_at+b±S_bt[X] at confidence interval 95%	r r^2 r^2%	t_{tab} at 95% Confidence interval	Calculated t-value $= \frac{\lvert r \rvert \sqrt{n-2}}{\sqrt{1-r^2}}$
0.01-0.1	229.52±3.95+350.06±64.08[X]	0.9747 0.9501 95.01%	2.262	12.35

Application:-

Two methods used for determination Hydrochloric acid (36.5-38.0%, country: U.S.A) in commercial samples. The methods were used firstly method was Linear Array Ayah 5SX1-T-1D-Continous flow injection analyzer[9].while the second method was PH meter. A series of variable concentration ranging from 0.05 to 0.08 mol.L^{-1} 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 commercial sample

Comparison between flow injection & classical methods (mol.L^{-1})	Paired Differences		t Cal. $t = \frac{\bar{x}_d \sqrt{n}}{\sigma_{n-1}}$	df	Sig. (2-tailed)	t critical at 95% confidence interval
	Mean $\bar{x}_d$	Std. Deviation				
0.05-0.08	**82.66**	**75.511**	**2.189**	**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 Copperion (II) by Hydronium ion from cation exchange column with potassium hexacyanoferrate (III) to form green dark precipitate as ion pair complex. The new method can be used to determine of Hydronium ion in pure and commercial samples without need for calibrated, solution buffer and electrodes. The precipitate is measured via the attenuation of incident light by Linear Array Ayah 5SX1-T-1D-Continous flow injection analyzer[9]. 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.

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