A Novel Semi Automated On-Line Determination of Oxonium Ion Via Precipitation Reaction Using a New Mode of Attenuated Measurement of Incident Light (0 – 180^o) by AYAH 5SX4-ST-5D Solar CFI Analyser.

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Abstract

Strong acids were determined via the precipitation reaction of loaded copper (II) ion on strong cation exchange resin which in turn reacts with potassium hyxacyano ferrate (II). The attenuation effect of formed precipitate $Cu_2 [Fe (CN)_6]$ on (0 -180^o) incident LED light was measurement via homemade AYAH 5SX4-ST-5D solar CFI analyser. Optimum parameters were 0.005M.L^{-1} $[Fe(CN)_6]^{-4}$, flow rate of 2.4 mL.min^{-1} , sample volume 204 µL , sample purge time of 64 seconds was chosen, and 1.6 V for light intensity. A liner calibration graph of 0.005 -0.2 M.L^{-1} were obtains for HCl, HNO_3, $HCLO_4$ and H_2SO_4, with a linearity (r^2 %) 96 -97 % and L.O.D based on gradual dilution of lowest concentration in calibration graph was 37.19 µg for HCl, 64.273 µg for HNO_3, 102.26 µg for $HCLO_4$, and 0.01 µg for H_2SO_4 .Repeatability (RSD %) less than 1.12 was obtained. the proposed was compared well with standard method. FTU method for available acid in commercial (HCl, H_2SO_4).

Keywords: Turbidity, Oxonium ion, ion exchange

تقدير نبيل اني شبه تلقائي لأيون الأوكسونيوم عن طريق تفاعل الترسيب بأستخدام نمط جديد لقياس توهين الضوء الساقط بزاوية (0–180°) بوساطة AYAH 5SX4–ST–5D solar CFI analyser

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الخلاصة

قدرت الحوامض القوية عن طريق تفاعل الترسيب والمعتمد على التفاعل بين ايون النحاس الثنائي والمحمل على مبادل ايوني حامضي قوي و بوناسيوم سداسي ثايوسيانات الحديد (II). قياس توهين الضوء المسلط بزاوية (0–180°) والمعتمد على تكوين راسب $Cu_2 [Fe (CN)_6]$ يتم عن طريق محلل الحقن الجرياني المستمر والمصنع محليا AYAH 5SX4–ST–5D solar CFI analyser. تم اختيار الظروف الفضلى 0.005مول.لتر$^{-1}$ $[Fe(CN)_6]^{-4}$ وسرعة الجريان 2.4 مل. دقيقة$^{-1}$ ،حجم الأنموذج المحقن 204مايكروليتر ،زمن حقن الأنموذج 64 ثانية ويالأضافة الى 1.6 فولت وهي شدة الضوء الساقط . منحني معايرة بحدود 0.005 – 0.2 مول .لتر$^{-1}$ لكل من HCl, HNO_3, $HClO_4$ بالأضاقة الى H_2SO_4 مع نسبة خطيه (r^2%) تمتد من 96– 97 % بالأضافة الى حدود الكشف (LOD) والمستندة على التخفيف

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التدريجي لأقل تركيز في منحني المعايرة 73.19ملغم لأنموذج HCl ، 64.273مكغم لـ HNO_3 ، 102.26
مكغم لـ $HClO_4$ بالأضافة الى 0.01 مكغم لـ H_2SO_4 . تم الحصول على تكرارية (RSD%) اقل من
1.12 .وقد تم مقارنة الطريقة المقترحة مع الطريقة الكلاسيكية لكل من الحوامض المتوفرة (HCl ، H_2SO_4).

1-Introduction

The word acid comes directly from the Latin word acidus, meaning "sour.", it was known to exist for hundreds of years before the time of Arrhenius, but no one had recognized their essential nature, in his studies of solutions, Arrhenius found the common acids [sulphuric acid (H_2SO_4(aq)), hydrochloric acid (HCl (aq)), nitric acid (HNO_3(aq)), and perchloric acid ($HClO_4$(aq))] were dissolved in water, virtually every molecule dissociates to give ions. These substances are strong electrolytes and are thus called strong acids . A strong acid is one that completely dissociates into its ions. Thus, if 100 molecules of HCl are dissolved in water, 100 H^+ ions and 100 Cl^- ions are produced. Virtually no HCl molecules exist in aqueous solution. Sulphuric acid is a special case. The formula H_2SO_4 indicates that this acid can produce two H^+ ions per molecule when dissolved in water. However, only the first H^+ ion is completely dissociated. Thus a solution of H_2SO_4 dissolved in water contains mostly H^+ ions and HSO_4^- ions. 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. Numerous methods available for acid determination wheel the using convectiveal PH meter [1], or spectrophotomtric method via the development of coloured product[2-5] for example formation of Br_2 (λ_{max} 381 nm) [6,7], or tri iodide ion (λ_{max}351 nm) [8] via the reactions BrO_3^- –Br^-- H_3O^+ or IO_3^- – I^-- H_3O^+ [8] system. Also chemiluminescence[9-12] was used for acid determination through the formation of Br_2 which reacted with H_2O_2 to formation peroxyl radical($HOO^{\cdot}$) necessary for(5-amino phthalhydrazide) oxidation and the generation chemiluminescence measured at 425nm[10]. Varies methods were used but it never came at the literature a turbidimetric method for acid determination .in this research a new approach was used for acid determination via the replacement of acid (hydronium ion) to exchenge with Cu(II) ion (loaded on stationary cation exchange resin) ,followed by reaction Cu(II) ion with potassium hexacyano ferrate (II) to formation $Cu_2[Fe(CN)_6]$ as a brown precipitate. This then can be measured with AYAH 5Sx4-ST-5D solar CFI analyser. In which four white snows LED was used as a radiation source light using solar cell as an energy transducer detector.

2-1 Chemicals & Reagents

All chemicals were used of analytical reagent grade while distilled water was used to complete the solution to mark. A standard solution of cupric nitrate trihydrate (0.1mol.L^{-1}) was prepared by dissolving 2.4160 g in 100mLdistilled water. A stock solution Potassium hexacyano ferrate (II) $K_4[Fe(CN)_6.3H_2O]$ (0.1mol.L^{-1}) was prepared by dissolving 21.1190 g in 500 mL of distilled water. Sulfuric acid solution (96%,1.84 g.mL^{-1}, BDH, 2mole.L^{-1} was prepared by pipetting 222.09mL of concentrated sulfuric acid and completed to the volume with distilled water to 2L of volumetric flask. Hydrochloric acid solution (38% 1.19 g.mL^{-1}, BDH, 2mole.L^{-1}) was prepared by pipetting 323mL of concentrated Hydrochloric acid and completed to the volume with distilled water to 2L of volumetric flask. Perchloric acid solution (60% 1.54 g.mL^{-1}, BDH, 2mole.L^{-1}) was prepared by pipetting 435.25mL of concentrated Perchloric acid and completed to the volume with distilled water to 2L of volumetric flask. Nitric acid solution (70% 1.42 g.mL^{-1}, BDH, 2mole.L^{-1}) was prepared by pipetting 253.64 mL of concentrated Nitric acid and completed to the volume with distilled water to 2L of volumetric flask. Each acids was standardized against sodium carbonate Na_2CO_3 solution (2mol.L^{-1}). Barium chloride $BaCl_2.2H_2O$ (Fluka, 0.1mol.L^{-1}) was prepared by dissolving 2.2442 g in 100mLdistilled water. Lead acetate (Fluka, 0.1mol.L^{-1})was prepared by dissolving 9.4883 g in 100mLdistilled water.

2-2 Apparatus

The flow gram used for the determination of of Oxonuim ion (H_3O^+) in acids, shown schematically in figure-1, two channels peristaltic pump variable speeds (Ismatec , Switzerland). Valve 6 – port medium pressure injection valve (I D E X corporati two channels on , USA) with sample loop (1 mm i.d. Teflon ,variable length) . the instrument response was measured by a homemade Ayah 5SX4-ST-5D Solar-CFI analyser, which uses five snow white LED for irradiation of the flow cell at 2mm path length(blue 474nm, green 530nm white 464nm, red 550 , pink).Four solar cell used as a detector for collecting signals via sample travelling for 60 mm length. The readout of the system composed of x-t potentiometric recorder (Kompenso Graph C-1032) Siemens (Germany) (1-500 mV) or digital AVO-meter (auto range) (0-2 volt) (China). Turbidometric readings under batch conditions were made by HANNA Company (Hungary).

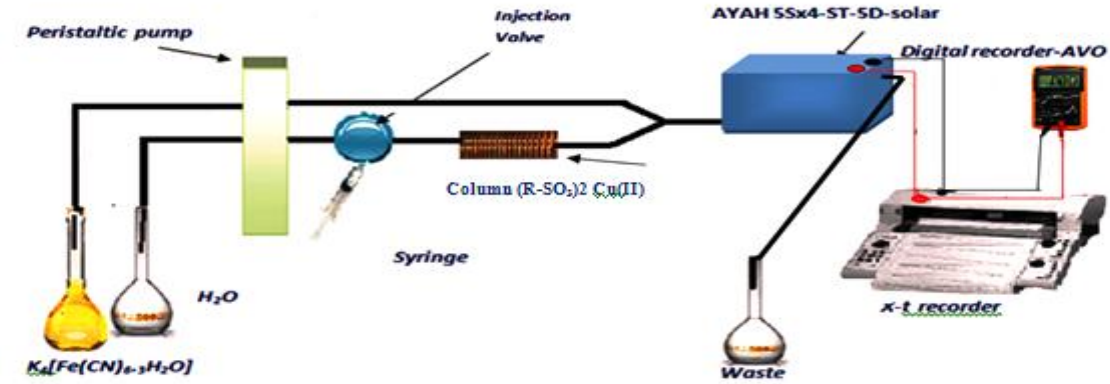

Figure 1- schematic diagram of flow injection analysis system for determination of Oxanium ion via ion exchange resin using AYAH SSx4-ST-5D-solar CFI analyzer

2-3 Resin preparation

An enough quantity of polymeric resin of the form $RSO_3\text{-}Na^+$ was taken in a 500 mL beaker, washed many times with distilled water to remove any dusty particles that might be present in the resin material. The clear beads of resin is treated with concentrated hydrochloric acid (0.1M) and kept a side covered with a witch class watch occasional a slight stirring may be needed.

$$RSO_3\text{-}Na^+ + HCl \longrightarrow RSO_3\text{-}H^+ + Na^+ + Cl^-$$

After few hours the resin was washed many times with distilled water until negative test with blue litmus paper. The resin is then transferred to a column (45 cm) packed well. Copper solution Cu (II) then passed through the column (flow rate = 1.7 mL.min^{-1}) And replacement Cu(II) ion to exchange with acid (hydronium ion) (loaded on stationary cation exchange resin).

$$2RSO_3\text{-}H_3O^+ + Cu\,(II) \longrightarrow (RSO_3)_2\text{-}\,Cu\,(II) + 2H_3O^+$$

2-4 Methodology

The manifold shown in figure-1 was used after a few trial of the adjusted chemical reaction. The manifold is composed of two lines; one line of potassium hexacyano ferret $[Fe(CN)_6]^{-4}$ 0.005 mol.L^{-1}) .while the second used line as carrier stream (distil water); that carriers the acid sample through the injection valve using fixed sample volume204, 2.4 ml.min^{-1} is the optimum flow rate, and 1.6V light intensity. The acid when reaches to the manifold; the elution of loaded Cu(II) ion from the resin, is commenced followed by the formation of brown precipitate with $[Fe(CN)_6]^{-4}$at the (Y-junction), which then can be measured with AYAH 5Sx4-ST-5D solar CFI using a snow white LED.

$$4H_3O^+ + 2\,(R\text{-}SO_3)_2Cu^{+2} \longrightarrow 4\,R\text{-}\,SO_3\text{-}H_3O^+ + 2\,Cu^{+2}$$

$$2Cu^{+2} + [Fe(CN)_6]^{-4} \longrightarrow \underset{\text{Brown ppt.}}{Cu_2[Fe(CN)_6.3H_2O]} + 2H_3O^+$$

3-Study of the optimum parameters

The manifold shown in figure-1 was employed for the optimization of chemical as well as physical variables. These variables were optimized using single variable optimization.

3-1 Chemical variables

3-1-1 Effect of $K_4[Fe(CN)_6.3H_2O]$ Concentration

Using variable concentration 0.001-0.2 mol.L^{-1}of potassium hexacyanoferrate$[Fe(CN)_6]^{-4}$, with sample volume 204µL for each of the acids used (*HCl , HNO_3 , H_2SO_4 and $HClO_4$*) 0.1mol.L-1, at 2.4 ml.min^{-1} flow rate and the intensity of incident light of LED expressed in voltage (1.6 V) were used. Table-1 summarizes the results obtained and figure-2 shows that 0.005mol.L^{-1} of $[Fe(CN)_6]^{-4}$ is the optimum concentration. An increase in concentration leads to increase in energy transducer response, but increase in concentration up to 0.005mol.L^{-1} leads to decrease in energy transducer response thus which might be attributed to increase precipitated particle, therefore; this causes a decrease in peak height and 0.005mol.L^{-1} was the optimum concentration for$[Fe(CN)_6]^{-4}$.

Table 1- Effect for the variation of $[Fe(CN)_6]^{-4}$ on the response of $[Fe(CN)_6]^{-4}$-Cu(II) on ionic exchange- H_3O^+ system

$[Fe(CN)_6]^{-4}$	HCl 0.1 mol.L^{-1}					$HNO_3$0.1 mol.L^{-1}				
Mol. L^{-1}	**Yi mV**	$\bar{Y}_i$ **mV**	S.D **σ_{n-1}**	RSD %	**$\bar{y}_{i} \pm t\,SEM$**	**Yi mV**	$\bar{Y}_i$ **mV**	S.D **σ_{n-1}**	RSD %	**$\bar{y}_{i} \pm t\,SEM$**
0.001	92 , 92 , 92	92	0	0	92 ± **0**	116, 112, 114	114	2	1.754	116 ± 4.96
0.003	100, 100,100	100	0	0	100 ± **0**	116,116 ,116	116	0	0	114± 0
0.005	332 ,332 , 332	332	0	0	332 ± **0**	316,316, 316	316	0	0	316± 0
0.01	328, 328 , 328	328	0	0	328 ± **0**	302,304 ,300	302	2	0.66	302± 4.96
0.05	292, 288 ,290	290	2	0.69	290±4.96	278,276, 280	278	2	0.72	278± 4.96
0.1	252, 252, 252	252	0	0	252 ± **0**	234,232 ,236	234	2	0.85	234± 4.96
0.15	216, 216 , 216	216	0	0	216 ± **0**	194,192, 196	194	2	1.03	194± 4.96
0.2	184, 184 , 184	184	0	0	184 ± **0**	164 ,168 , 166	166	2	1.20	166± 4.96
0.3	144, 144 ,144	144	0	0	144 ± **0**	140, 136 , 138	138	2	1.44	138± 4.96
$[Fe(CN)_6]^{-4}$	$HClO_4$ 0.1 mol.L^{-1}					H_2SO_4 0.1 mol.L^{-1}				
mol L^{-1}	**Yi mV**	$\bar{Y}_i$ **mV**	S.D **σ_{n-1}**	RSD %	**$\bar{y}_{i} \pm t\,SEM$**	**Yi mV**	$\bar{Y}_i$ **mV**	S.D **σ_{n-1}**	RSD %	**$\bar{y}_{i} \pm t\,SEM$**
0.001	88, 88, 88	88	0	0	114 ± 0	116, 112, 114	114	2	1.7	114± 4.96
0.003	116, 112, 114	114	2	1.75	88 ± 4.96	124 , 128 , 126	126	2	1.6	126± 4.96
0.005	30, 304 , 304	304	0	0	304± 0	280 , 280, 280	280	0	0	208± 0
0.01	264, 264, 264	264	0	0	264± 0	264 , 268 , 266	266	2	0.7	114± 4.96
0.05	260 ,256 , 258	258	2	0.77	258± 4.96	260 ,256, 258	258	0	0	280± 0
0.1	200, 196, 198	198	2	1.01	198± 4.96	252 , 248 , 250	250	2	0.8	250± 4.96
0.15	160 ,156 ,158	158	2	1.26	158± 4.96	236, 232, 234	234	2	0.8	234± 4.96
0.2	140, 136, 138	138	2	1.44	138± 4.96	200, 200, 200	200	0	0	200± 0
0.3	116, 116, 116	116	0	0	116± 0	172 , 172 ,172	172	0	0	172± 0

* **SEM= $\sigma_{n-1}/\sqrt{n}$** * **t = $t_{0.05/2, n-1}$ = 4.303 , $\bar{n}$=3 $y_{i\pm t\,SEM}$ =** Confidence interval at (95%)

$\bar{Y}_i$ = **attenuation** of incident light expressed as Average peak height (n=3) in (mV)

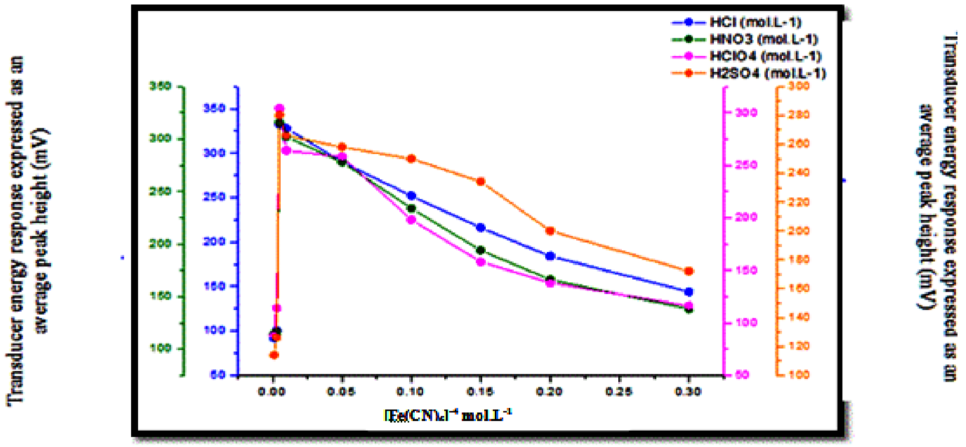

Figure 2- Effect of$[Fe(CN)_6]^{-4}$ in moll^{-}on transducer attenuation response via the attenuation light for determination of Oxonium ion versus^1

3-2-Physical variables

3-2-1- Effect of flow rate

Using optimum concentration of the reactant, $[Fe(CN)_6]^{-4}$.0.005mol.L^{-1},and sample volume 204µl with a variable range(0.8 to 3.8 ml.min^{-1}) of flow rate was used for both line. Figure-3 shows that the best flow rate for the completion of the precipitate of Cu(II) by $[Fe(CN)_6]^{-4}$. is 2.4 mL.min^{-1} for both of lines in flow injection system figure-1. The results obtained were summarized in table-2 and table-3. It was noticed at slow flow rate, there is increase in dilution and dispersion which might be leads to an increase in base width Δt_B of response, while at higher flow rate (>2.4 ml.min^{-1}) although the effect on physical parameter was not very crucial on the height of response ; obtaining regular response and sharp maxima but it is a decrease in peak high due to settling rate of precipitate particulates from measuring cell prior to completion of reaction. Therefore; a flow rate of 2.4ml.min^{-1} was a chosen as optimum flow rate for H_3O^+ determination to obtain a maximum response.

Table 2- Effect for the variation of Flow rate on the response of $[Fe(CN)_6]^{-4}$-Cu(II) on ionic exchange- H_3O^+ system

Flow rate	HCl 0.1 mol.L^{-1}					HNO_3 0.1 mol.L^{-1}				
ml.min^{-1}	**Yi mV**	$\overline{Y_i}$ mV	s.D σ_{n-1}	RSD %	$\bar{y}_{i} \pm t\,SEM$	**Yi** mV	$\overline{Y_i}$ mV	s.D σ_{n-1}	RSD %	$\bar{y}_{i} \pm t\,SEM$
0.8	612, 612 , 612	612	0	0	$612_{\pm 0}$	448 ,448, 448	448	0	0	$448_{\pm 0}$
1.8	504, 504 504	504	0	0	$504_{\pm 0}$	356, 352, 354	354	2	0.56	$278_{\pm 4.96}$
2.4	464, 464, 464	464	0	0	$464_{\pm 0}$	352, 348, 350	350	2	0.57	$384_{\pm 4.96}$
3	452, 456, 454	454	2	0.44	$454_{\pm 4.96}$	328 ,328, 328	328	0	0	$360_{\pm 0}$
3.8	440 ,440 ,440	440	0	0	$440_{\pm 0}$	300, 296, 298	298	2	0.67	$338_{\pm 4.96}$
Flow rate	$HClO_4$ 0.1 mol.L^{-1}					H_2SO_4 0.1 mol.L^{-1}				
ml.min^{-1}	**Yi** V	$\overline{Y_i}$ mV	s.D σ_{n-1}	RSD %	$\bar{y}_{i} \pm t\,SEM$	**Yi** V	$\overline{Y_i}$ mV	s.D σ_{n-1}	RSD %	$\bar{y}_{i} \pm t\,SEM$
0.8	424 ,424, 424	424	0	0	$424_{\pm 0}$	292 ,292, 292	292	0	0	$292_{\pm 0}$
1.8	380, 376 ,378	378	2	0.53	$278_{\pm 4.96}$	256 ,252 ,254	254	2	0.79	$254_{\pm 4.96}$
2.4	384, 384, 384	384	0	0	$384_{\pm 0}$	232, 232, 232	232	0	0	$232_{\pm 0}$
3	360, 360 ,360	360	0	0	$360_{\pm 0}$	212, 212, 212	212	0	0	$212_{\pm 0}$
3.8	340, 336, 338	338	2	0.59	$338_{\pm 4.96}$	180, 180, 180	180	0	0	$180_{\pm 0}$

*** SEM= $\sigma_{n-1}/\sqrt{n}$, $t = t_{0.05/2,\ n-1} = 4.303$, $n= 3$**

$\bar{\bar{y}}_{i} \pm t\,SEM$ = Confidence interval at (95%) , Y_i = **attenuation** of incident light expressed as Average peak height (n=3) in (mV)

Table 3-effect of variation flow rate on peak widths of the obtained response

FLOW Rate mL.min^{-1}	Δt_B ***HCl sec***	Δt_B ***HNO_3 sec***	Δt_B ***$HClO_4$*** sec	Δt_B ***H_2SO_4 sec***
0.8	**90**	**96**	**69**	**90**
1.8	**54**	**48**	**45**	**51**
2.4	**42**	**42**	**36**	**33**
3	**30**	**30**	**30**	**24**
3.8	**24**	**27**	**27**	**18**

Δtb (sec):- peak base width.

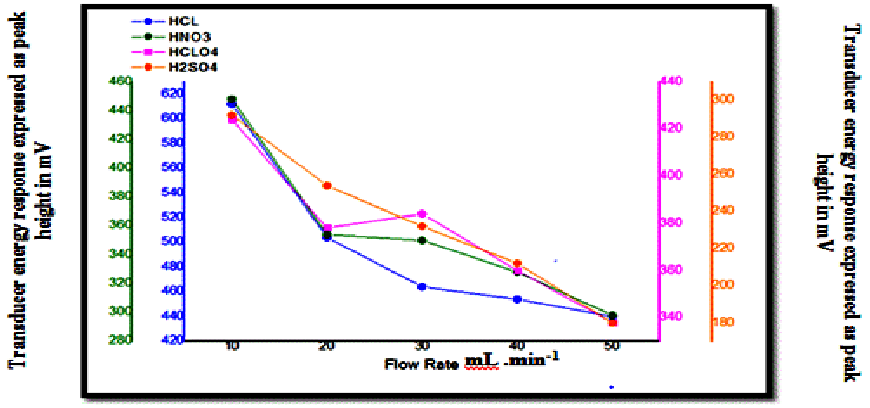

Figure 3- Effect of Flow rate on transducer attenuation response via the attenuation light for determination of Oxonium ion

3-2-2 Sample volume

Using the optimum flow rate of 2.4 mL.min^{-1} with a various loop volumes (38-280) µL via the use of various loop length for sample introduction using open valve mode i.e. allowance for continuous purge of sample from the sample loop in the injection valve. Table-4 and table-5 tabulate the injected sample volume, with response obtained each sample was measured three times successively. The data obtained were plotted as depicted in figure-4, showing that the optimum sample volume was 204 µl gave a regular response. The increase of sample segment (more than 204 µl) probably might increase the time duration of sample segment in front of the detector which might probably cause the irregular flow of two factor i.e the load for the carrier stream to carry on thus causing a reverse movement of precipitate particles causing abroad of the maxima peak which indicate the increase of precipitate particles in front of detector which leads to attenuated of incident light to reach in the detector therefore the sample volume of 204 is the optimum for near studied as shown in figure-4, and figure-5 shown response profile of variation of sample volume for incident light intensity.

Table 4-Effect for the variation of sample volume on the response of $[Fe(CN)_6]^{-4}$-Cu(II) on ionic exchange-H_3O^+ system

sample volume		**HCl 0.1 mol.L^{-1}**					**HNO$_3$ 0.1 mol.L^{-1}**				
Loop length cm	µL	**Yi mV**	**$\overline{Y_i}$ mV**	s.D **σ_{n-1}**	RSD %	**$\bar{y}_{i\pm t\,SEM}$**	**Yi mV**	**$\overline{Y_i}$ mV**	s.D **σ_{n-1}**	RSD %	**$\bar{y}_{i\pm t\,SEM}$**
5 cm ,0.7mm	38	16, 16, 16	16	0	0	$16_{\pm 0}$	12 ,12 , 12	12	0	0	$12_{\pm 0}$
10cm ,0.7mm	76	40 , 40 , 40	40	0	0	$40_{\pm 0}$	24 , 26 , 25	25	1	4	$25_{\pm 2.48}$
12cm , 0.7mm	92	52 ,52 , 52	52	0	0	$52_{\pm 0}$	32, 32 , 32	32	0	0	$32_{\pm 0}$
10.9cm ,1mm	171	64, 64 ,64	64	0	0	$64_{\pm 0}$	40 , 40 ,40	40	0	0	$40_{\pm 0}$
26.55cm ,0.mm	204	252, 248 , 250	250	2	0.8	$250_{\pm 4.96}$	176 ,172 , 174	174	2	1.149	$174_{\pm 4.96}$
17.85cm , 1mm	280	124, 122 ,123	123	1	0.813	$123_{\pm 2.48}$	80 , 80 ,80	80	0	0	$80_{\pm 0}$
Sample volume		**HClO$_4$ 0.1 mol.L^{-1}**					**H$_2$SO$_4$ 0.1 mol.L^{-1}**				
Loop length cm	µL	**Yi mV**	**$\overline{Y_i}$ mV**	s.D **σ_{n-1}**	RSD %	**$\bar{y}_{i\pm t\,SEM}$**	**Yi mV**	**$\overline{Y_i}$ mV**	s.D **σ_{n-1}**	RSD %	**$\bar{y}_{i\pm t\,SEM}$**
5 cm ,0.7mm	38	20, 16 , 18	18	2	1.11	$18_{\pm 4.96}$	10 ,10 , 10	10	0	0	$10_{\pm 0}$
10cm ,0.7mm	76	40, 36, 38	38	2	5.26	$38_{\pm 4.96}$	24, 24 , 24	24	0	0	$24_{\pm 0}$
12cm , 0.7mm	92	68 ,68 , 68	68	0	0	$68_{\pm 0}$	28, 28, 28	28	0	0	$28_{\pm 0}$
10.9cm ,1mm	171	80, 80 , 80	80	0	0	$80_{\pm 0}$	36 ,36, 36	36	0	0	$36_{\pm 0}$
26.55cm ,0.mm	204	260 ,256 158	158	2	1.26	$158_{\pm 4.96}$	148, 144 , 146	146	2	1.34	$146_{\pm 4.96}$
17.85cm , 1mm	280	124 ,120 ,122	122	2	1.64	$122_{\pm 4.96}$	72, 72, 72	72	0	0	$72_{\pm 0}$

$^*\overline{SEM} = \sigma_{n-1}/\sqrt{n}$, * $t = t_{0.05/2,\, n-1} = 4.303$, $n = 3$, $y_{i\pm t\,SEM}$ = Confidence interval at (95%), Y_i = attenuation of incident light expressed as Average peak height (n=3) in (mV)

Table 5-Effect of variation of sample volume on peak widths

Loop length cm	*Sample volume µL*	*Δt_B HCL sec*	*Tim Sec.*	*Δt_B HNO_3 sec*	*Tim Sec.*	*Δt_B $HCLO_4$ sec*	*Tim Sec.*	*Δt_B H_2SO_4 sec*	*Tim Sec.*
5 cm ,0.7mm	**38**	**12**	**64**	**12**	**60**	**15**	**66**	**15**	**64**
10cm ,0.7mm	**76**	**15**	**62**	**18**	**64**	**15**	**62**	**21**	**64**
12cm , 0.7mm	**92**	**9**	**72**	**21**	**64**	**18**	**72**	**18**	**62**
10.9cm ,1mm	**171**	**12**	**72**	**15**	**68**	**21**	**72**	**15**	**72**
26.55cm ,0.mm	**204**	**27**	**64**	**21**	**64**	**33**	**68**	**30**	**64**
17.85cm , 1mm	**280**	**18**	**64**	**18**	**64**	**30**	**64**	**33**	**62**

Δtb (sec):- peak base width.
t (sec) :- arrival time of the injected sample from the valve till leave the flow measuring cell

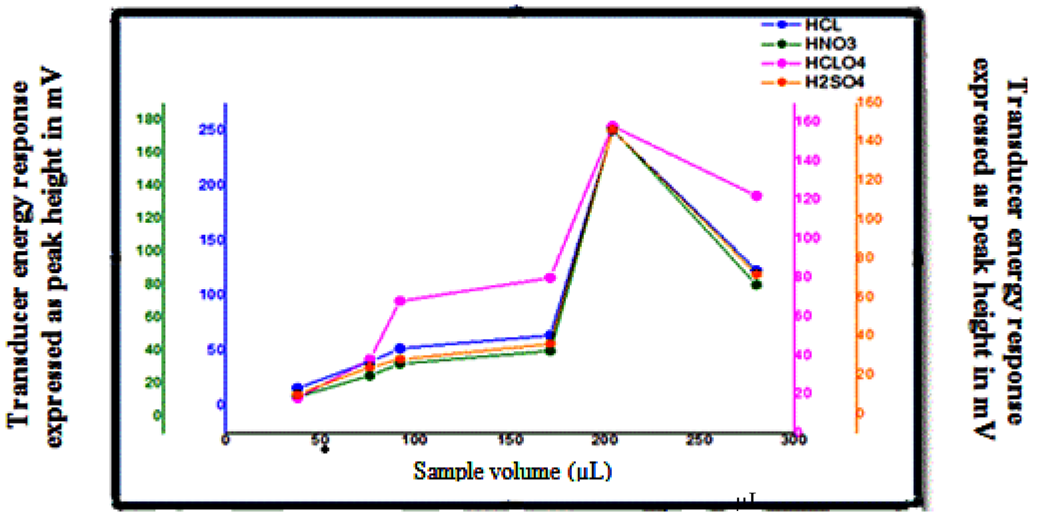

Figure 4- Effect of sample volume on transducer attenuation light for determination of Oxonium ion

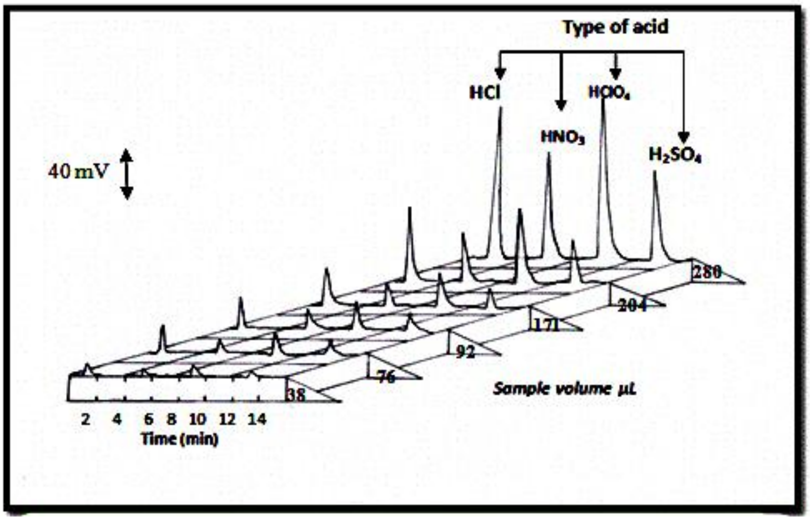

Figure 5- Response profile versus time for variations sample volume by using hydronium (HCI, H_2SO_4, $HCIO_4$ and HNO_3) with conc. 0.1 moLL^{-}

3-2-3-Purge time

Variable purge times were used for the sample segment of (10-50) seconds were used for this study in addition to open valve mode. Time for the carrier solution to pass through the injection valve while it is in the injection mode followed by turning the injection valve to the load position was studied. Sample volume 204µL and 1.6V light intensity was used with concentration 0.005mol.L^{-1} of $[Fe(CN)_6]^{-4}$. Table-6 tabulate the purge time, Each was repeated for three times successively figure 6 shows the continuation of the increase in transducer energy response with increase of injection time up to 64 seconds (open valve) followed by a relatively constant response in a height of responses. Therefore; open valve a purge time was chosen as optimum time to the complete purge of the sample from sample loop.

Table 6- Effect for the variation of purge time on the response of $[Fe(CN)_6]^{-4}$-Cu(II) on ionic exchange- H_3O^+ system

purge time	HCl 0.1 $mol.L^{-1}$					HNO_3 0.1 $mol.L^{-1}$				
Sec.	**Yi mV**	$\bar{Y}_i$ **mV**	s.D σ_{n-1}	RSD %	$\bar{y}_{i\pm t\,SEM}$	**Yi mV**	$\bar{Y}_i$ **mV**	s.D σ_{n-1}	RSD %	$\bar{y}_{i\pm t\,SEM}$
10	20 , 20 , 20	20	0	0	$20_{\pm 0}$	12, 12, 12	12	0	0	$12_{\pm 0}$
20	32 , 32 , 32	32	0	0	$32_{\pm 0}$	20 , 20 ,20	20	0	0	$20_{\pm 0}$
30	80, 80 , 80	80	0	0	$80_{\pm 0}$	40 ,40, 40	40	0	0	$40_{\pm 0}$
40	164, 164 , 164	164	0	0	$164_{\pm 0}$	68 , 68 ,68	68	0	0	$68_{\pm 0}$
50	240, 236 , 238	238	2	0.84	$238_{\pm 4.96}$	116, 116 , 116	116	0	0	$116_{\pm 0}$
open	268, 264 ,266	266	2	0.75	$266_{\pm 2.67}$	160 , 156 ,158	158	2	1.26	$168_{\pm 4.96}$
purge time	$HClO_4$ 0.1 $mol.L^{-1}$					H_2SO_4 0.1 $mol.L^{-1}$				
Sec.	**Yi mV**	$\bar{Y}_i$ **mV**	s.D σ_{n-1}	RSD %	$\bar{y}_{i\pm t\,SEM}$	**Yi mV**	$\bar{Y}_i$ **mV**	s.D σ_{n-1}	RSD %	$\bar{y}_{i\pm t\,SEM}$
10	10 , 10 , 10	10	0	0	$10_{\pm 0}$	8 , 8 , 8	8	0	0	$8_{\pm 0}$
20	32 , 32 , 32	32	0	0	$32_{\pm 0}$	24 , 24, 24	24	0	0	$24_{\pm 0}$
30	68, 68 , 68	68	0	0	$68_{\pm 0}$	60 ,60 , 60	60	0	0	$60_{\pm 0}$
40	136, 136 , 136	136	0	0	$136_{\pm 0}$	72 , 72 , 72	72	0	0	$72_{\pm 0}$
50	160, 160 , 160	160	0	0	$160_{\pm 0}$	92 , 92 , 92	92	0	0	$92_{\pm 0}$
open	176 , 172 , 174	174	2	1.15	$174_{\pm 4.96}$	164, 160 , 162	162	2	1.23	$162_{\pm 4.96}$

* SEM= $\sigma_{n-1} / \sqrt{n}$ * t = $t_{0.05/2}$, n-1 =4.303 n =3

$\bar{y}_{i\pm t\,SEM}$ = Confidence interval at (95%)

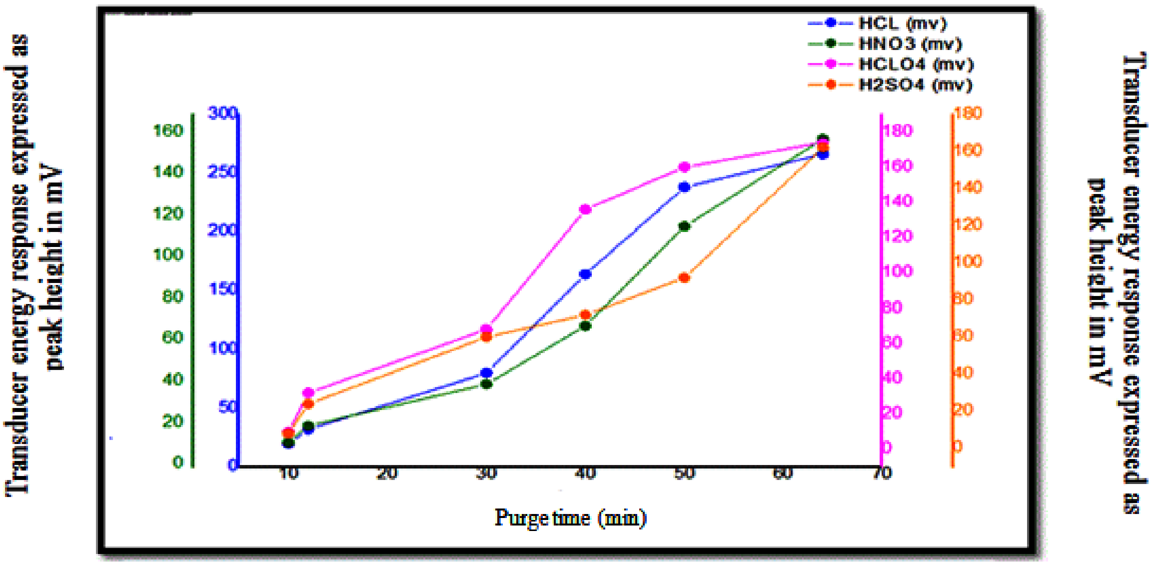

Figure 6- Effect of purge time transducer attenuation response via the attenuation light for determination of Oxonium ion

3-2-4-Incident light intensity

Intensity of light source was studied using the optimum physical and chemical parameters achieved in previous sections, with 0.005 mol.L^{-1} $[Fe(CN)_6]^{-4}$. Variable intensity of light source expressed in voltage (0.1-2) volt by variation of light intensity channel in Ayah 5SX4-ST-5D Solar CFI Analyser operation where read by AVO-meter. The results tabulated in table-7 which shows that an increase on the attenuation of incident light by precipitate particles of $Cu_2[Fe(CN)_6]_2$ with increased intensity of source light. The intensity of 1.6 volt was selected as the optimum voltage that can be supplied to give a better transducer energy response as shown in figure-7.

Table 7-Effect for the variation of intensity light on the response of $[Fe(CN)_6]^{-4}$-Cu(II) on ionic exchange-H_3O^+ system

intensity light	HCl 0.1 mol.L^{-1}					HNO$_3$ 0.1 mol.L^{-1}				
volt	**Yi mV**	**$\overline{Yi}$ mV**	s.D **σ_{n-1}**	RSD %	**$\overline{y}_{i\pm t\,SEM}$**	**Yi mV**	**$\overline{Yi}$ mV**	s.D **σ_{n-1}**	RSD %	**$\overline{y}_{i\pm t\,SEM}$**
0.1	32, 32, 32	32	0	0	$32_{\pm 0}$	20 , 20 , 20	20	0	0	$20_{\pm 0}$
0.6	96, 96, 96	96	0	0	$96_{\pm 0}$	56, 56, 56	56	0	0	$56_{\pm 0}$
1	168, 168, 168	168	0	0	$168_{\pm 0}$	100, 96, 98	98	2	2.04	$98_{\pm 4.96}$
1.6	272, 276, 274	274	2	0.73	$274_{\pm 4.96}$	156, 156, 156	156	0	0	$156_{\pm 0}$
1.8	268, 272, 270	270	2	0.74	$270_{\pm 4.96}$	152, 148, 150	150	2	1.33	$150_{\pm 4.96}$
2	92, 96, 96	94	1,15	1.23	$94_{\pm 2.86}$	48, 48, 48	48	0	0	$48_{\pm 0}$
intensity light	HClO$_4$ 0.1 mol.L^{-1}					H$_2$SO$_4$ 0.1 mol.L^{-1}				
volt	**Yi mv**	**$\overline{Yi}$ mv**	s.D **σ_{n-1}**	RSD %	**$\overline{y}_{i\pm t\,SEM}$**	**Yi mv**	**$\overline{Yi}$ mv**	s.D **σ_{n-1}**	RSD %	**$\overline{y}_{i\pm t\,SEM}$**
0.1	28, 28, 28	28	0	0	$28_{\pm 0}$	12 , 12 , 12	12	0	0	$12_{\pm 0}$
0.6	84, 88, 86	86	2	2.33	$86_{\pm 4.96}$	40, 40 ,40	40	0	0	$40_{\pm 0}$
1	144, 144, 144	144	0	0	$144_{\pm 0}$	72 , 72 ,72	72	0	0	$72_{\pm 0}$
1.6	232, 228, 230	230	2	0.87	$230_{\pm 4.96}$	124, 124 ,124	124	0	0	$124_{\pm 0}$
1.8	228, 228, 228	228	0	0	$228_{\pm 0}$	120 ,120 , 120	120	0	0	$120_{\pm 0}$
2	80, 76 ,78	78	2	2.56	$78_{\pm 4.96}$	40 , 40 , 40	40	0	0	$0_{\pm 0}$

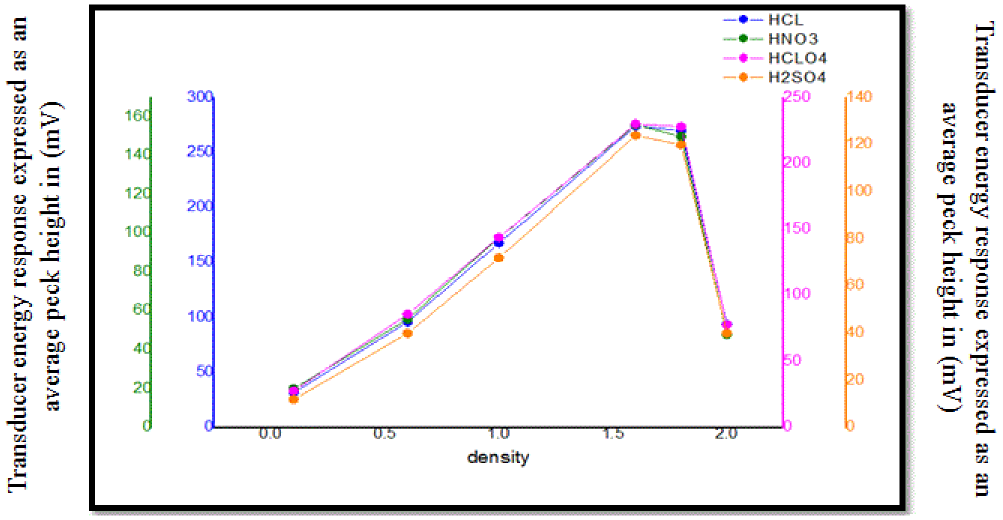

Figure 7- Variation for incident light intensity on attenuation of incident light

4-Calibration graph

A series of different acids (*HCl* , *H_2SO_4* , *$HClO_4$ and HNO_3*) solutions ranging from(0.005 to 0.2) mol.L^{-1} for each acid were prepared and injected at the established optimum condition. A scatter plot diagram was constructed between the variations of the energy transducer responses versus concentration of acids showing a linear dynamic range from 0.005 - 0.15 mol.L^{-1}. Table-.8 tabulate the correlation coefficient , linear percentage , straight line equation and the calculated t-value at 95% confidence which larger than tabulated t-value indicating clearly that the linearity against non-linearity is accepted.

Table 8-Summary of linear regression for the variation of energy tranducer response with acids concentration using simple regression line of the from ($\hat{Y}$ = a+bx) at optimum conditions.

Type of acid	***Measured] [H_3O^+] mol.L^{-1}***	***Linear dynamic range [H_3O^+] mol.L^{-1} n= 9***	***$\hat{y}$= a ± S_at + b ± S_bt [X] at confidence interval at 95%, n-2***	***r r^2 %***	***t_{table} no. at 95%, n-2***	Calculated t-value = $\frac{/r/\sqrt{n-2}}{\sqrt{1-r2}}$
HCl	0.005-0.2	0.005-0.15	15.932±56.026+3667.61±593.541 [x]	0.9808 96.02%	2.306<< 17.235	
HNO_3	0.005-0.2	0.005-0.15	-13.4152 ±46.342+3469± 490934 [x]	0.9805 96.14%	2.306 << 11.443	
$HClO_4$	0.005-0.2	0.005-0.15	21.395 *±36.116+3491.65 ± 382.604 [x]*	0.9882 97.65%	2.306 << 8.561	
H_2SO_4	0.005-0.2	0.005-0.15	-8.003*±17.097+ 2263.355 ±181.111 [x]*	0.993 97.73%	2.306<< 9.671	

$\hat{Y}$(mV) =Estimated response for (n=3), [x]= ***[H_3O^+]*** conc.(mol.L^{-1}), r=correlation coefficient, r^2%:linearity percentage

5-Limit of detection

Three different approaches were used.Gradual dilution of lowest concentration in the calibration graph, or detection based on the numerical value of slope and from the linear regression plot. Table-9 tabulates all these calculated values of detection limit for 204 µL sample solution.

Table 9-Limit 0f detection for acids at optimum parameter

Type of acid	*Practically based on the gradual dilution for the minimum concentration*	*Theoretical based on the volume of slope* $X= 3S_B / slope$	*Based on the linear equation* $y=y_B +3S_B$ ^
HCl	*37.19 µg*	*60.84 ng*	204.09 *µg*
HNO_3	*64.273 µg*	*0.111 µg*	532.7 *µg*
$HClO_4$	*102.26 µg*	*0.1760 µg*	657.720 *µg*
H_2SO_4	*0.0100 µg*	*0.2652 µg*	468.939 *µg*

S_B: standard deviation of blank solution. , X= value of L.O.D based on slope.
Y_B: average response for the blank solution (equivalent to intercept in straight line equation).
L.O.D = limit of detection.

5-Repeatability

The repeatability of measurement and the efficiency of homemade Ayah 5SX4-ST-5D Solar CFI analyser were studied at fixed concentrations from one of acid (HCl- H_2SO_4-$HClO_4$-HNO_3) 0.1mol.L^{-1} using the optimum parameters. Repeated measurements for eleven successive injections were measured and obtained results are tabulated in Table-10 which shows that the percentage relative standard deviation was less than 1%. Figure-8-A, B, C, D shows a kind of response-time profile for the used concentrations.

Table 10-Repeatability of successive measurements for acids at 0.1mol.L^{-1}conc. , 204 µL

Type of acid	No. of times injection to **acid** 0.1mol. L^{-}	Incident light response expressed as peak height (mV)	Average $\bar{y}_i$ mV	Standard deviation σ_{n-1}	Repeatability RSD %	confidence interval of the mean $\bar{y} \pm t_{0.05/2,\, n-1}\, \sigma_{n-1} / \sqrt{n}$
HCl	11	212,212,212,212,208,212,212 , 212, 208,212 , 208,	210	1.87	0.89	210 ± 1.254
HNO_3	11	*160,160,160,160,160,164,164, 160, 160,160, 164,*	*161*	*1.87*	*1.16*	*161.09 ± 1.254*
$HCLO_4$	11	*252,252,252,252,252,256,252, 252, 252,256, 252*	*252*	*1.61*	*0.64*	*252.727 ± 1.0795*
H_2SO_4	11	*156,156,160,156,156,156,156, 156, 160,160, 156*	*157*	*1.87*	*1.12*	*157.09 ± 1.254*

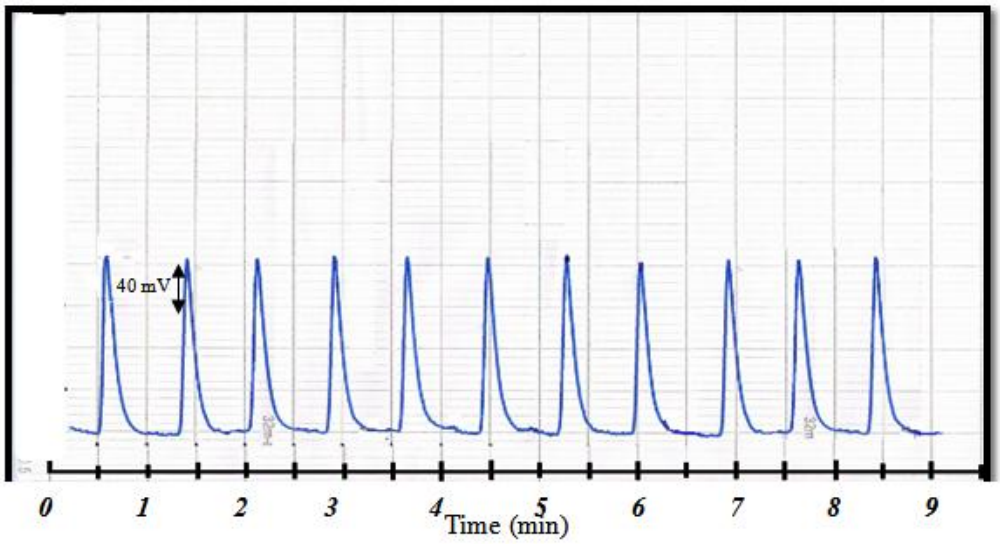

Figure 8- (A) successive Response profile for variation Repeatability if incident light to 204uL HCI

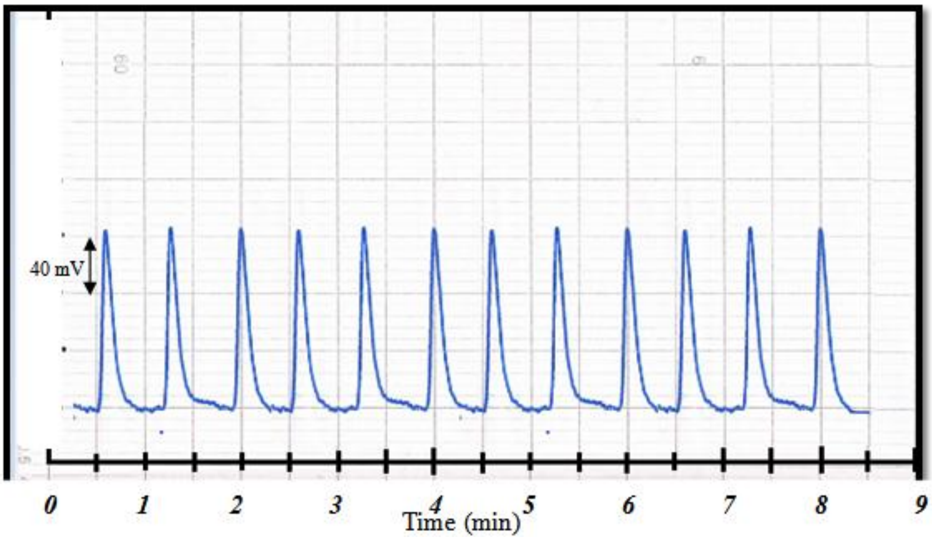

Figure 8-(B) successive Response profile for variation Repeatability incident light to 204 uL HNO_3

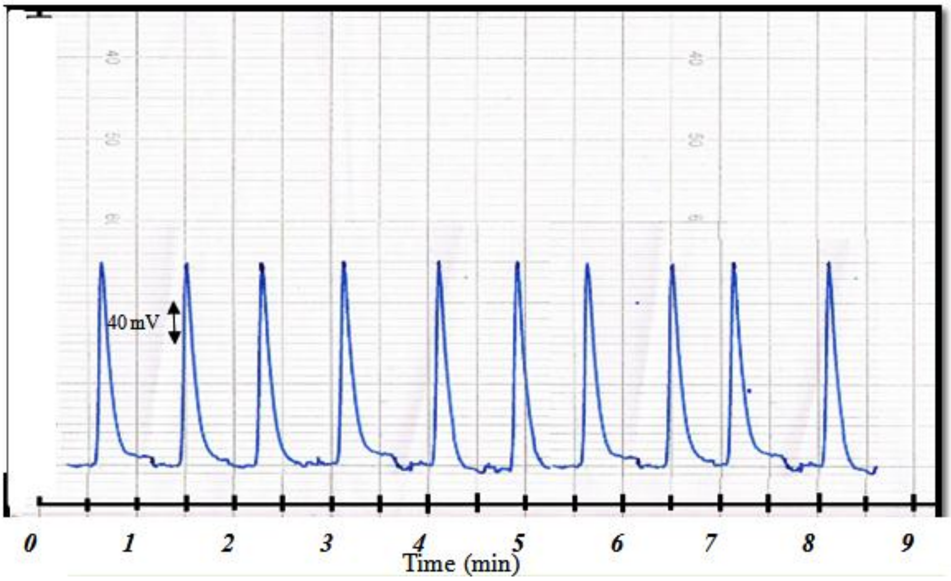

Figure 8- (C) successive Response profile for Repeatability variation of incident light to 204 uL $HCIO_4$

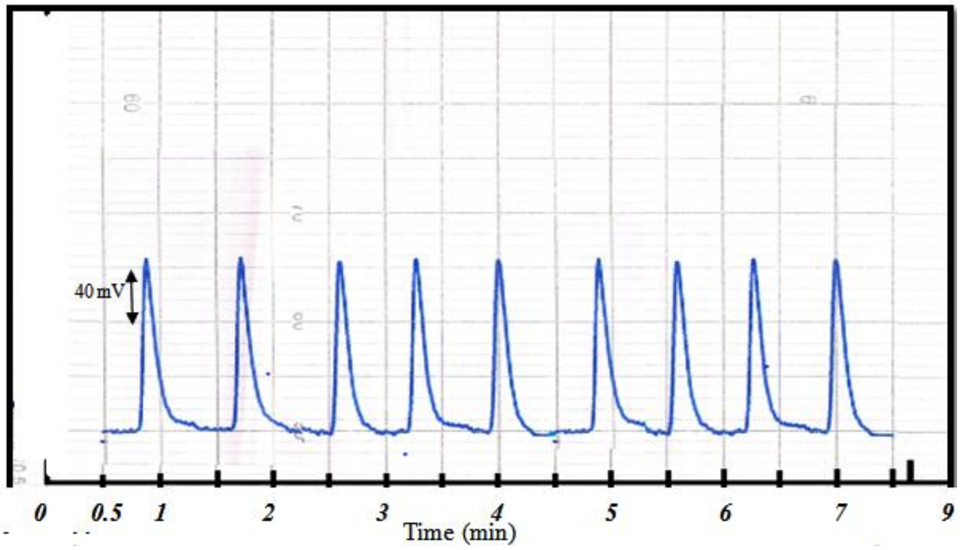

Figure 8- (D) successive Response profile for variation Repeatability of incident light to uL H_2sO_4

6-Analysis of sample preparation:

Two methods were used to determination H_3O^+ in different acids (HCl-BDH, H_2SO_4-BDH). Firstly using Ayah 5SX4-ST-5D solar CFI analyser while the second method was used the classical measurement for turbidity (Turbidity- HANNA). A series of solutions for each acids was prepared by transferring (0.12- 5.1 ml)for HCl and 0.06- 2.5ml for H_2SO_4(1.964 mol.L^{-1}) to ten volumetric flask (25ml) to obtain (0.005- 0.2) mol.L^{-1}for each acids. Table-1 tabulates the summed up for series concentration method results from each acids using classical method. The established method was used for the determination H_3O^+ in two sample (HCl- J. T. Baker- India, H_2SO_4- Lobachemie. - India) using Ayah 5SX4-ST-5D solar CFI analyser and was compared with classical method via the measurement (HANNA- Hungary). a comparison between two methods as shown in table-12-A series of solution from each acids were prepared by transferring (0.125- 5 ml)for HCl (2mol.L^{-1}), 0.03- 1.2 ml for H_2SO_4 (2 mol.L^{-1}), to ten volumetric flask (50ml) to obtain (0.005- 0.2) mol.L^{-1}, (0.001- 0.05) mol.L^{-1} for HCl, H_2SO_4 respectively ; followed by addition 1ml from lead acetate (0.1 mol.L^{-1}) for samples which contained HCl, while addition 1ml for barium chloride (0.1 mol.L^{-1}) to samples contained H_2SO_4 solution [13] .The result summarized in table-13, shows the measurements were conducted by both methods using paired t- test. Results were mathematically treated for calibration graph at confidents level of 95% (α =0.05). Paired t-test was used as shown.

Table.11-Summary of linear regression for the variation of turbidity with acids, Concentration using simple regression line of the from ($\hat{Y}$ = a+bx) classical, Method via HCl- Pb (II) and H_2SO_4 – Ba(II) systems**.**

Type of acid	***Measured $[H_3O^+]$ mol.L^{-1}***	***Linear dynamic range $[H_3O^+]$ mol.L^{-1} n***	***$\hat{y}= a \pm S_a t + b \pm S_b t\ [X]$ at confidence interval at 95%, n-2***	***r r^2 %***	***t_{tab} at 95%, n-2***	Calculated $t_{\text{-value}} = \frac{/r/\sqrt{n-2}}{\sqrt{1-r_2}}$	***L.O.D mmol.L^{-1}***
HCl	0.005-0.2	0.005-0.2	3.34±5.1723 + 414.17± 54.795[x]	0.987 97.4%	2.306 <<17.4297		2.5
H_2SO_4	0.001-0.05	0.001-0.01	2.128± 0.602+ 603.272± 101.01[x]	0.986 97.3%	2.447<<14.613		0.5

$\hat{Y}$= turbidity [FTU] , [x] = $[H_3O^+]$ mol.L^{-1} , FTU = formazine turbidity unite

Calibration graph of classical method (measurement of turbidity) was made to the determination of $[H_3O^{+1}]$ in acids (HCl- H_2SO_4) from 0.005-0.2 mol.L^{-1}, table -12-A, B shows the comparison between both methods . The results indicated that the proposed method was more sensitive than the classical method.

Table 12 A- Summary of result compared between Classical method & present method to HCl

Ayah 5SX4-ST-5D solar analyzer FIA	Classical method HCl	Analytical parameter
97.79	97.4	r^2%:linearity percentage
0.005-0.2	0.005-0.2	Linear range mol.L^{-1}
3667.61mV/mmol.L^{-1}	424.17 FTU/mmol.L^{-1}	Sensitivity (b)
15.932 mV	3.34 FTU	Intercept (a)
37.190 µg /sample	911.5 µg/Sample	practical Limit of detection
204 µl	5 ml	Sample volume
< 1%	2.5%	Repeatability (n=5)RSD%

Table 12 B- Summary of result compared between Classical method & present method to H_2SO_4

Ayah 5SX4-ST-5D solar analyzer FIA	Classical method H_2SO_4	Analytical parameter
97.3	97.3	r^2%:linearity percentage
0.005-0.2	0.005-0.2	Linear range mol.L^{-1}
2263.355 mV/mmol.L^{-1}	603.272 FTU/mmol.L^{-1}	Sensitivity (b)
-8.0036 mV	2.128 FTU	Intercept (a)
0.0100 µg /sample	2452 µg/Sample	practical Limit of detection
204 µl	5 ml	Sample volume
< 1%	2.5%	Repeatability (n=5)RSD%

FTU: Formazine turbidity unit

Table 13- paired t –test results for Ayah 5SX4 –ST-5 D solar CFI analyser (proposed method) with classical method using A series of solution for determination of H_3O^+ in different acids.

Type of acids , compny	A moment found □ (mol.L^{-1}) at Confidence level 95%			X d mol.L^{-1}	□ d mol.L^{-1}	σ_{n-1}	t_{cal} = □d $\sqrt{n}$ / σ_{n-1} at 95%	t $_{tab}$ at 95%
	Theoretical conc. µ	Proposed method Ayah 5SX4 –ST-5Dsolar CFI analyser	Turbidity meter Method (HANNA)					
HCl J. T. Baker-India	0.05 0.07 0.1	0.041 0.063 0.12	0.058 0.076 0.12	0.017 0.013 0.00	0.01	0.01	1.732 << 4.303	
H_2SO_4 Lobachemie. - India	0.05 0.07	0.031 0.075	0.09 0.103	0.04 0.028	0.034	0.008	6.01<< 12.706	

Table-13shows the comparison between two methods, it was found that there was significant difference between calculated value and standard value in addition to no significant between two methods for determination of oxonium ion in samples due to calculated t-value less than tabulated t-value ($t_{0.05/2}$,2 = 4.303, $t_{0.05/2}$,1= 12.7) at 25% confidence level.

7-Conclusion

Different acids can be determined using turbidimetric based sequence of reaction, the resin used satisfies more than 100 successive injection. The proposed method uses cheaper instrument and reagents. In this paper a more effective faster determination was achieved by ayah 5SX4-ST-5D solar cell CFI analyser, light emitting diode as source with a detection using solar cell. The standard addition method was used to avoid matrix effects. Also this method can be applied to micro determination of H_3O^+ in pure as well as in different acids.

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