

# A NOVEL METHOD FOR THE DETERMINATION OF [H<sub>3</sub>O<sup>+</sup>] ION IN WEAK ACIDS VIA CONTINUOUS FLOW INJECTION AND 532NM SOLID STATE LASER DIODE

Issam MA Shakir<sup>1\*</sup> and Ali Q Jameel<sup>2</sup>

<sup>1</sup>Department of Chemistry, College of Science,  
University of Baghdad, Baghdad-Iraq.

<sup>2</sup>Department of research and quality control,  
Oil lines pipes Company, Ministry of oil, Baghdad-Iraq.

## ABSTRACT

The proposed method is simple, sensitive and rapid for the determination of Hydronium ion in weak acids using 532nm solid state laser diode with continuous flow injection analysis and using laser dye (Rhodamine6G) as a fluorescent host. The method was based on the fluorescence of Rhodamine6G and quenching effect of fluorescence by weak acid in aqueous medium. A linear range of weak acid was 0.9-1000mMol.L<sup>-1</sup> for H<sub>3</sub>PO<sub>4</sub>, 9-2000mMol.L<sup>-1</sup> for CH<sub>3</sub>COOH and 100-2000mMol.L<sup>-1</sup> for HCOOH, with correlation coefficient  $r = 0.9775, 0.9524$  and  $0.9724$ , successively the limit of detection (LOD) was 31.484, 192.941 and 190.150  $\mu\text{g/sample}$  based on gradual dilution of lowest concentration in calibration graph. Chemical and physical parameters of this system were investigated. The method can be regarded as an alternative analytical way of determining acids.

**Keywords:** Weak acids, Rhodamine6G, Fluorescence.

## 1. INTRODUCTION

A weak acid is only partially ionized in their solutions, releasing only some of its hydrogen atoms into the solution<sup>1</sup>. Thus it is less capable than a strong acid of donating protons. Most acids are weak acids. Examples of weak acids include acetic acid, formic acid, phosphoric acid and ascorbic acid<sup>2,3</sup>. Some of the most commonly used methods for determination of weak acids include ion chromatography<sup>4,5</sup>, acid-base titration<sup>6</sup>, gas chromatographic<sup>7,8</sup>, volumetric methods<sup>9</sup> and gas permeation flow injection analysis<sup>10</sup>. Rhodamine6G is used as a laser dye, or gain medium, in dye lasers<sup>11,12</sup> and is pumped by the 2nd (532 nm) harmonic from an Nd:YAG laser. The dye has a remarkably high photostability, high fluorescence quantum yield, low cost, and its lasing range has close proximity to its absorption maximum (approximately 530 nm)<sup>13,14</sup>. The emission range of the dye is 555 to 585 nm with a maximum at 566 nm. Rhodamine6G usually comes in three different forms<sup>15</sup>. Rhodamine6G chloride is a bronze/red powder, highly soluble<sup>16</sup>, this formulation is very corrosive to all metals except stainless steel. Other formulations are less soluble, but also less corrosive. Rhodamine6G perchlorate comes in the form of red crystals, while Rhodamine6G tetrafluoroborate appears as maroon crystals<sup>17,18</sup>. Fluorescence is a phenomenon that occurs when a substance absorbs radiation of a certain wavelength, or group of wavelengths, and re-emits photons of different wavelength. When certain compounds absorb light, an electron is excited to a higher vibrational energy state. The molecule then loses its excess of vibrational energy by collisions and falls to the lowest vibrational level of the energy state. In addition, almost all molecules occupying an energy state higher than the second undergo internal conversion and pass from the lowest vibrational level of the upper state to a higher vibrational level of a lower state which has the same energy<sup>19</sup>. From there, the molecules again lose energy until the lowest energy level of the first excited state is reached. From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence<sup>20,21</sup>.

## 2. Experimental

### 2.1. Reagents and chemicals

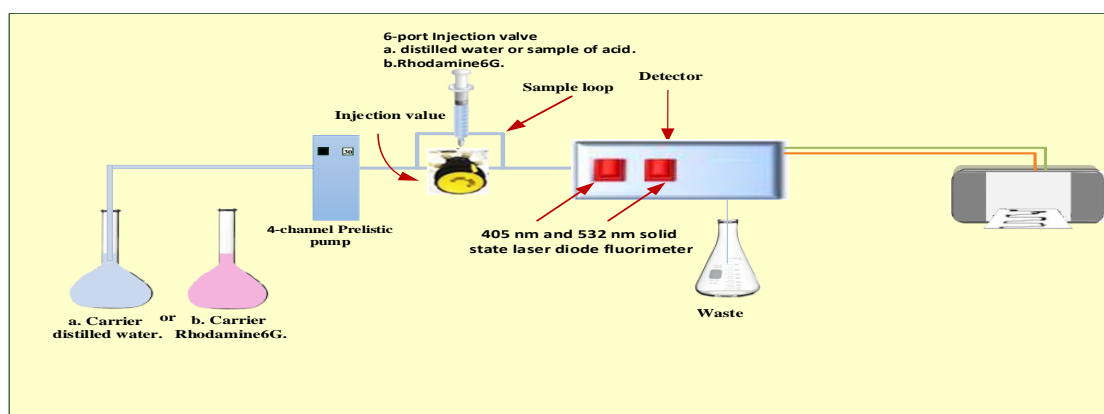
A stock solution ( $0.01 \text{ Mol.L}^{-1}$ ) of Rhodamine6G ( $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$ , M.wt479.02  $\text{g.mol}^{-1}$ ) was prepared by dissolving 2.3951g in 500 ml of distilled water. A stock solutions of acids orthophosphoric acid (88%w/w,  $1.75 \text{g.ml}^{-1}$ , BDH,  $2 \text{Mol.L}^{-1}$ ) acetic acid (99.5%w/w,  $1.05 \text{g.ml}^{-1}$  BDH,  $2 \text{Mol.L}^{-1}$ ) and formic acid (98%,  $1.220 \text{g.ml}^{-1}$ , J.T.B aker,  $2 \text{Mol.L}^{-1}$ ) was prepared by pipetting 127.28ml, 114.96ml, 77ml and respectively of concentrated acids and complete the volume with distilled water to 1000 ml volumetric flasks. Each acid was standardized against standard solution from NaOH (BDH,  $40 \text{g.mol}^{-1}$   $0.1 \text{Mol.L}^{-1}$ ); which prepared by dissolving 1g in 250 ml distilled water.

### 2.2. APPARATUS

Laser diode fluorimeter is a homemade instrument that is capable in measuring fluorescence at 405(10mW), and 532nm(not less than 1000mW) laser diode. Both radiation source is fitted with a 2mm flow cell in a block of brass metal equipped with a photo diode detector. The angle between the radiation source at an aperture of 2mm a maximum radiation area for a flow cell having outside diameter 4mm inside diameter 2mm (path length for absorption of irradiation) is  $90^\circ$ . The schematic diagram in figure no.1 shows the system used, which comprises the use peristaltic pump four channels, variable speed (Ismatec type ISM 796), A rotary 6-port injection valve (Rheodyne, U.S.A) with a sample loop (id 1 mm, Teflon, Variable length) used for sample injection. The output signals was recorded by x-t potentiometric recorder (KOMPENSO GRAPH C-1032) Siemens (Germany). UV-VIS Spectrophotometer digital double beam (type UV-1800, Shimadzu, Japan) was also used to scan the spectrum of colored species using Quartz cell.

### 2.3. Methodology

The general procedure will be the use of 532nm solid state diode laser (green laser) as it will be discussed for creation of various different studies that will be adopted (e.g.; variable studies) scatter plot was first to made followed by selecting the calibration curve most acceptable level of correlation coefficient decided by the researcher and the outcome of the obtained data from the measurements. Every signal measurement was repeated for three successive times. Repeatability and limit of detection were carried out. Three different acids were studied Phosphoric, acetic, and Formic as weak acids. The flow diagram of the whole reaction manifold system used for the determination of Hydronium ion in weak acids by the reaction between weak acids and Rhodamine6G to fluorescence quenching. The carrier stream (Rhodamine6G) ( $1.1 \times 10^{-4} \text{Mol.L}^{-1}$ ) at  $2 \text{mL.min}^{-1}$  flow rate to react with the injected sample volume ( $459 \mu\text{L}$ ) weak acids and carry the mixture to complete the reaction. This segment passes through flow measuring cell. The response profile of which was recorded on x-t potentiometric recorder to measure quenching of fluorescence expressed as peak height in mV. Figure (1) shows the flow gram that was used for the determination the hydronium ion in weak acids.



**Fig. 1: A schematic diagram of manifold used in the determination of acid via either quenching of released fluorescence (Continuous mode) or inhibition of fluorescence (Discrete mode).**

### 3.1. Chemical variables and Physical variable<sup>22</sup>

#### 4. Calibration graph of weak acids

##### 4.1. Calibration graph of Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)

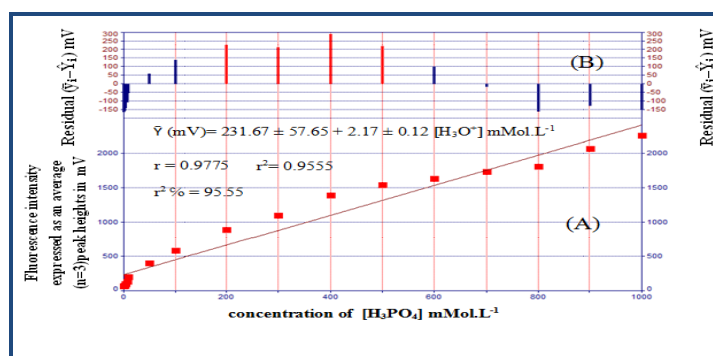
A series of Phosphoric acid solutions ranging from (0.9 to 2000) mMol.L<sup>-1</sup> were prepared from a stock solution having the concentration of 2Mol.L<sup>-1</sup> in distilled water and injected at the established optimum conditions (c.f. section 3). The first range used (0.9-2000) which gave a correlation coefficient  $r = 0.8890$  with an explained values for all data given to be 79.04%. This is regarded a weak correlation for equation used  $Y = a + bx$ . While the second range used (0.9-1000) which gave a value of  $r = 0.9775$  with an ability to explain about 95.55% of the data taken by the chosen linear equation. Therefore the second calibration range can be used. A sample of fluorescence intensity vs time profile can be seen in figure no. (5).

**Table 1: Scatter plot data for Phosphoric acid (i.e.; all measured data were used)**

Concentration of H <sub>3</sub> PO <sub>4</sub> in distilled water (mMol.L <sup>-1</sup> )	$\bar{Y}_i$ mV	S.D $\sigma_{n-1}$	RSD %	$\bar{Y} \pm t \text{ sem}$
0.9	70	0	0	70 ± 0
1	70	0	0	70 ± 0
3	80	0	0	80 ± 0
5	100	1	1	100 ± 2.49
8	140	1	0.71	140 ± 2.49
10	200	0	0	200 ± 0
50	400	0	0	400 ± 0
100	585	5	0.85	587 ± 12.44
200	893	11.55	1.29	893 ± 28.73
300	1100	5	0.45	1100 ± 12.44
400	1393	11.55	0.83	1393 ± 28.73
500	1540	5	0.32	1540 ± 12.44
600	1633	11.55	0.71	1633 ± 28.73
700	1733	10	0.58	1733 ± 24.87
800	1807	11.55	0.64	1807 ± 28.73
900	2060	5	0.24	2060 ± 12.44
1000	2253	10	0.44	2253 ± 24.87
1200	1690	10	0.59	1680 ± 24.87
1500	1980	1	0.05	1980 ± 2.49
1800	2200	0	0	1800 ± 0
2000	2400	0	0	1800 ± 0

**Table 2: Range of the used concentration for Phosphoric acid**

Range of used concentration (mMol.L <sup>-1</sup> )	Correlation coefficient (r)	r <sup>2</sup> %
0.9-2000	0.8890	79.04
0.9-1000	0.9775	95.55



**Fig. 2: Calibration graph obtained from Scatter plot for the variation of H<sub>3</sub>PO<sub>4</sub> concentration on: A- Fluorescence intensity, B- residual ( $\bar{Y}_i - \hat{Y}_i$ )**

#### 4.2. Calibration graph of Acetic acid (CH<sub>3</sub>COOH)

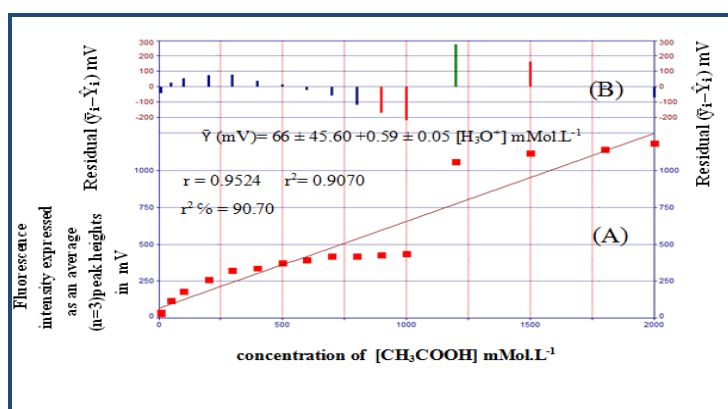
A stock solution of acetic acid (2Mol.L<sup>-1</sup>) in distilled water brings him to a series of acetic acid solutions ranging from (9 to 2000) mMol.L<sup>-1</sup> and injected at the established optimum condition (c.f. section 3). Since all data are involved with relatively good correlation value of  $r = 0.9524$ . These value will be regarded as scatter plot and calibration curve for equation used  $Y = a + bx$ . A sample of fluorescence intensity vs time profile can be seen in figure no. (5).

**Table 3: Scatter plot data for acetic acid (i.e.; all measured data were used)**

Concentration of CH <sub>3</sub> COOH in distilled water (mMol.L <sup>-1</sup> )	$\bar{Y}$ mV	S.D $\sigma_{n-1}$	RSD%	$\bar{Y} \pm t \text{ sem}$
9	30	0	0	30 ± 0
10	40	0	0	40 ± 0
50	120	0	0	120 ± 0
100	180	0	0	180 ± 0
200	258	2.89	1.12	258 ± 7.19
300	320	0	0	320 ± 0
400	340	0	0	340 ± 0
500	377	5.77	1.53	377 ± 14.35
600	397	5.77	1.45	397 ± 14.35
700	420	0	0	420 ± 0
800	420	0	0	420 ± 0
900	428	3.46	0.81	428 ± 8.61
1000	440	0	0	440 ± 0
1200	1055	5	0.47	1055 ± 12.44
1500	1115	5	0.45	1115 ± 12.44
1800	1138	2.89	0.25	1138 ± 7.19
2000	1180	0	0	1180 ± 0

**Table 4: Range of the used concentration for Acetic acid**

Range of used concentration (mMol.L <sup>-1</sup> )	Correlation coefficient (r)	r <sup>2</sup> %
9-2000	0.9524	90.70



**Fig. 3: Scatter plot and calibration graph for the variation of CH<sub>3</sub>COOH concentration on: A- Fluorescence intensity, B- residual  $(\bar{y}_i - \bar{Y}_i)$**

#### 4.3. Calibration graph of Formic acid (HCOOH)

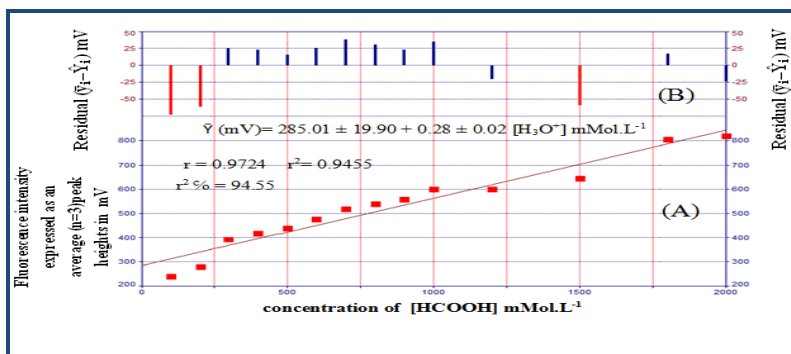
A stock solution of citric acid (2Mol.L<sup>-1</sup>) in distilled water brings him to a series of formic acid solutions ranging from (10 to 2000) mMol.L<sup>-1</sup> and injected at the established optimum condition (c.f. section 3). The first range used (10-2000) which gave a correlation coefficient  $r = 0.9379$  with an explained values for all data given to be 87.97%. This is regarded a little correlation for equation used  $Y = a + bx$  from the second and third range. An improvement of linearity of  $\approx 0.7\%$  was obtained for concentration range 100-2000 mMol.L<sup>-1</sup>. This difference can accommodate the use of 200-2000 mMol.L<sup>-1</sup> concentration range with no noticeable difference in sensitivity or loss of linearity. Therefore both calibration ranges (second or third) can be used. A sample of fluorescence intensity vs time profile can be seen in figure no. (5).

**Table 5: Scatter plot data for formic acid (i.e.; all measured data were used)**

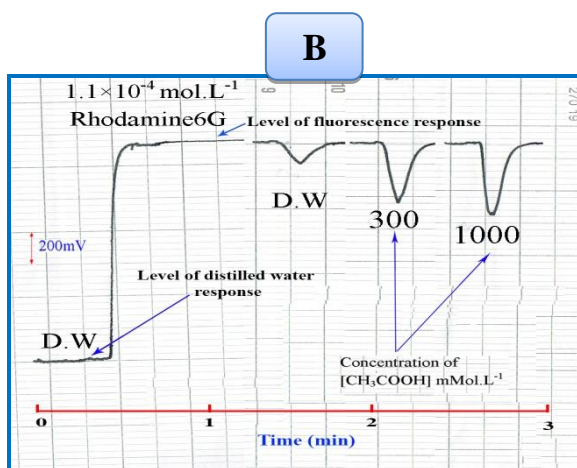
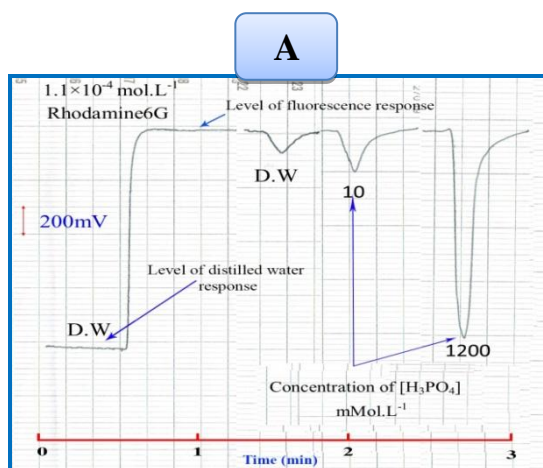
Concentration of HCOOH in distilled water (mMol.L <sup>-1</sup> )	$\bar{Y}_i$ mV	S.D $\sigma_{n-1}$	RSD %	$\bar{Y} \pm t \text{ sem}$
10	30	0	0	30 ± 0
20	80	0	0	80 ± 0
50	140	0	0	140 ± 0
100	240	0	0	240 ± 0
200	280	0	0	280 ± 0
300	395	5	1.26	395 ± 12.44
400	420	0	0	420 ± 0
500	440	0.58	0.13	440 ± 1.44
600	479	1.16	0.24	479 ± 2.89
700	519	1.16	0.22	519 ± 2.89
800	540	0	0	540 ± 0
900	560	0	0	560 ± 0
1000	600	0	0	600 ± 0
1200	600	0	0	600 ± 0
1500	645	5	0.78	645 ± 12.44
1800	805	5	0.62	805 ± 0
2000	820	0	0	820 ± 0

**Table 6: Range of the used Concentration for Formic acid**

Range of used concentration (mMol.L <sup>-1</sup> )	Correlation coefficient (r)	r <sup>2</sup> %
10-2000	0.9379	87.97
100-2000	0.9724	94.55
200-2000	0.9758	95.21



**Fig. 4: Calibration graph1 obtained from Scatter plot for the variation of HCOOH concentration on: A-Fluorescence intensity, B- residual ( $\bar{y}_i - \hat{Y}_i$ )**



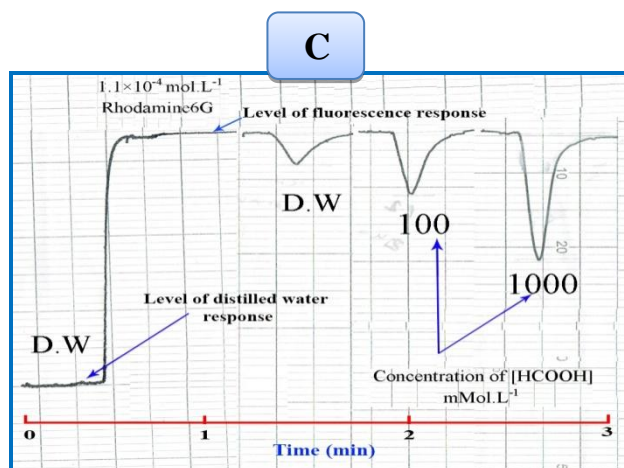


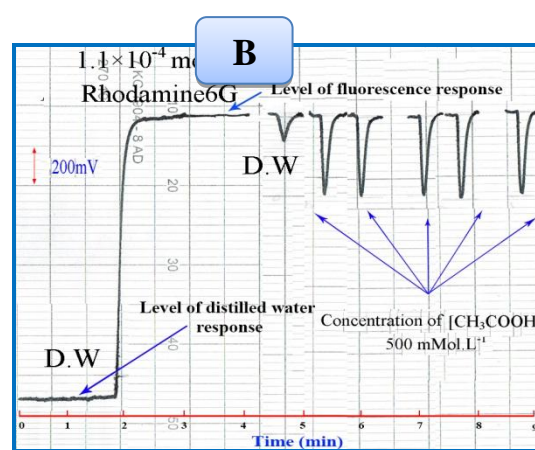
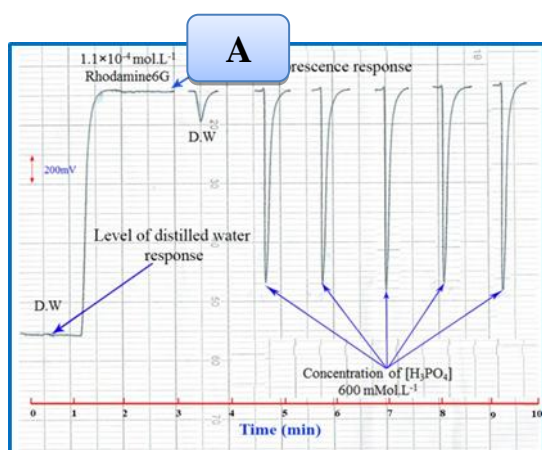
Fig. 5: Effect of variation of  $[H_3O^+]$  concentration  $mMol.L^{-1}$  (A- $H_3PO_4$ , B- $CH_3COOH$  and C- $HCOOH$ ) on response time profile

#### 4.4.Repeatability of weak acids

Fivesuccessive injected samples measurements were carried out for repeatability study for the determination of three weak acids [ $H_3PO_4$ ,  $CH_3COOH$  and  $HCOOH$ ] respectively was 600,500and 600  $mMol.L^{-1}$  via measurements of the Fluorescence intensity quenching. Table no.(7) show the results obtained, while Figure no.(6) shows a kind of quenching of fluorescence -time profile for the used concentrations.

Table 7: Repeatability of acids determined via the quenching of fluorescence

Type of acids	No. of times injection to acid $600 mMol.L^{-1}$	Fluorescence intensity quenching expressed as peak height (mV)	Average $\bar{y}$ mV	Standard deviation S.D	Repeatability RSD%	confidence interval of the mean
$H_3PO_4$	5	1620,1640,1640, 1620,1620	1628	10.95	0.67	$1628 \pm 13.57$
$CH_3COOH$	5	300,300, 300, 300,310	302	4.47	1.48	$302 \pm 5.54$
$HCOOH$	5	480,480, 480, 480,485	481	2.24	0.47	$481 \pm 2.776$



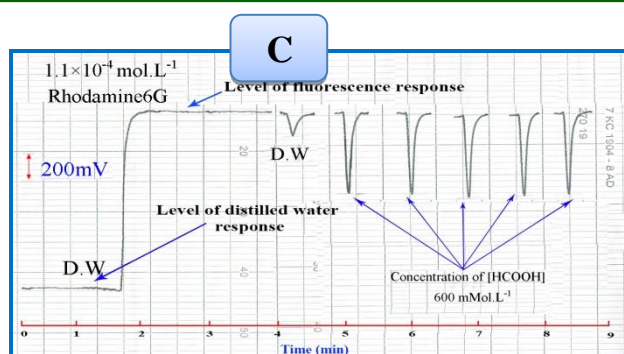


Fig. 6: A Profile of successive repeatability measurements of acids (A:  $\text{H}_3\text{PO}_4$ , B:  $\text{CH}_3\text{COOH}$ , C:  $\text{HCOOH}$  using 532nm solid state laser diode)

#### 4.5. Limit of detection for weak acids

The limit of detection of ( $\text{H}_3\text{O}^+$ ) was determined using the gradual dilution of the lowest concentration of the analyte in the calibration graph and based on the value of slope obtained from the linear regression plot as tabulated in table no.(8).

Table 8: Limit of detection for acids at optimum condition

Type of acid	$K_a$ for acids	Molecular weight of acids g/mol	minimum concentration ( $\text{mMol.L}^{-1}$ )	Practically based on the gradual dilution for the minimum concentration	Theoretical based on the volume of slope $X = 3S_B / \text{slope}$
$\text{H}_3\text{PO}_4$	$7.52 \times 10^{-3}$	97.99	0.7	31.484 $\mu\text{g/sample}$	139.285 $\mu\text{g/sample}$
$\text{CH}_3\text{COOH}$	$1.76 \times 10^{-5}$	60.05	7	192.941 $\mu\text{g/sample}$	313.937 $\mu\text{g/sample}$
$\text{HCOOH}$	$1.77 \times 10^{-4}$	46.03	9	190.150 $\mu\text{g/sample}$	507.066 $\mu\text{g/sample}$

$S_B$ : standard deviation of blank solution. ,  $X$ = value of L.O.D based on slope. L.O.D = limit of detection.

#### CONCLUSION

Laser diode fluorimeter– CFIA method is proposed for determination of ( $\text{H}_3\text{O}^+$ ) ion in weak acid and its characterized by simplicity, speed and accuracy. Repeatable measurement can be made easily giving a complete confidence in the assay method. Therefore the developed method can be regarded as an alternative simple method for the determination of Hydronium ion in weak acids.

#### REFERENCES

- Miessler GL and Tarr DA. Inorganic Chemistry (2nd ed., Prentice-Hall 1998;170) ISBN 0-13-841891-8.
- GB/T 1628.5-2000. Determination of formic acid in acetic acid by gas chromatography.
- Montgomery HAC, Dymock JF and Thom NS. The rapid colorimetric determination of organic acids and their salts in sewage-sludge liquor. The Analyst. 1962;87:949.
- Magne V, Mathlouthi M and Robilland B. Food Chem. 1998;61:449-453.
- Guillen DA, Barroso CG, Zorro L, Carrascal V and Perez-Bustamante JA. Analysis 1998;26:186-189.
- Narong Lenghor, Jaroon Jakmune, Michael Vilen, Rolf Sara and Gary D. Christian and Kate Grudpan. J Talanta. 2002;58:1139-1144.
- Cvijin P, Vujkovic D and Atkinson G. Applied spectroscopy. 1988;42:770-774.
- Wittman G, Van Langenhov H and Dewulf J. J chromatogr A. 2000;874:225-234.
- Chi Hung Tazang, RuoYuna and Mengsu Yang. J Biosensors and Bioelectronics. 2001;16:211-219.
- Tavatesn Araujo C, Lirade Carvalho J, Ribeiro Mota D, de Araujo CL and Coelho NMM. J food chemistry. 2005;92:765-770.
- Schäfer FP (Ed.), 1990 Dye Lasers, 3rd Ed. (Springer-Verlag, Berlin,).
- Duarte FJ and Hillman LW. (Eds.) 1999, Dye Laser Principles (Academic, New York,).
- Birge RR. "Kodak Laser Dyes," Kodak publication JJ. 1987;169.
- Starchura S and Allison J. Identification of organic pigments in automotive coatings using laser desorption mass spectrometry. J Forens Sci. 2007;52(3):595-603.
- Snavely BB. Continuous-Wave Dye Laser I, in Topics in Appl Phys. 1989;1.
- Drexhage KH. Structure and properties of laser dyes, Laser Focus. 1973;3:35-36.
- Drexhage K. Dye Lasers, Edited by F P Schafer, Springer-Verlag, Berlin. 1990;167-173.
- Brackmann U. Lambda chrome Laser Dyes, Lambda Physik, Germany. 1994;27-213,.

19. Basic Photophysics, Antonie JWG and Visserand Olaf J. Rolinski Laboratory of Biochemistry, Micro spectroscopy Centre Wageningen University, P.O. Box 8128 6700 ET Wageningen, The Netherlands.
20. Putterman SJ, Weninger KR. Sonoluminescence: How Bubbles Turn Sound into Light. *Annu Rev Fluid Mech.* 2000;32:445–476.
21. Sauer M, Hofkens J and Enderlein J. *Handbook of Fluorescence Spectroscopy and Imaging.* Wiley-VCH Verlag GmbH and KGaA Co. Weinheim, Germany. 2011;18-20.
22. Issam MA, Shakir Ali and Jameel Q. A Novel Method for the Determination of [H<sub>3</sub>O<sup>+</sup>] Ion in Strong Acids Via Continuous flow injection and 532nm solid state laser diode. Published in *International Journal of Researches in Pharmacy and Chemistry (IJRPC).* 2016;120-136.