



New Approach for an On-Line Turbidimetric Determination of Cadmium (II) in Different River Water Via the Use of A homemade Ayah 6SX1-T-2D Solar-Continuous Flow Injection Analyser

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Abstract

A newly developed analytical method characterized by its speed and sensitivity for the determination of cadmium (II) in aqueous solution in three randomly chosen samples from river water at different locations via turbidimetric measurement by Ayah 6SX1-T-2D Solar - CFI analyser. The method is based on the formation of yellowish white precipitate for the complex $Cd_3[Fe(CN)_6]_2$ by direct reaction of the cadmium (II) with potassium hexacyano ferrate (III) in aqueous medium. Turbidity was measured via the reflection of incident light that collides on the surfaces precipitated particles at $0-180^\circ$. Chemical and physical parameters were investigated. Linear dynamic of cadmium (II) is ranged from $0.05-12 \text{ mmol.L}^{-1}$, with correlation coefficient $r = 0.9951$. The limit of detection 25.29 ng/ sample from the step wise dilution for the minimum concentration in the linear dynamic range of the calibration graph with RSD % lower than 1.5% for 8 mmol.L^{-1} ($n=5$) concentration of cadmium (II). The method was applied successfully for the determination of cadmium (II) in three river samples. A comparison was made between the proposed method of analysis with the classical method (HANNA instrument for turbidity measurement) using the standard additions method via the use of ANOVA-treatments. It was noticed that there is a significant difference at $\alpha=0.05$ between the two methods at level < 0.05 was obtained. On that basis the new method can be accepted as an alternative analytical method.

Keywords: cadmium (II), spectrophotometry, Turbidity, flow injection analysis

نمط جديد لقياس التعكرية الأني لتقدير ايون الكاديوم في مختلف مياه الانهر من خلال محلل جديد مصنع محليا للحقن الجرياني المستمر (Ayah 6SX1-T-2D Solar).

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الخلاصة

تم تطوير طريقه تحليلية جديدة ، تميزت بالسرعة والحساسية لتقدير ايون الكاديوم الثاني في المحاليل المائية لثلاث نماذج عشوائية الاختبار من مياه الانهر ولمواقع مختلفة عن طريق قياس التعكرية بواسطة محلل الحقن الجرياني المستمر Ayah 6SX1-T-2D Solar. استندت الطريقة على تكوين راسب ابيض مصفر للمعدن $Cd_3[Fe(CN)_6]_2$ بواسطة التفاعل المباشر لايون الكاديوم (II) مع بوتاسيوم سداسي سيانيد الحديدك $K_3[Fe(CN)_6]$ في وسط مائي. تم قياس التعكرية عن طريق انعكاس الضوء المسلط والمصطدم بسطوح

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دقائق الراسب بزواوية 0-180°. تم دراسة كافة المتغيرات الفيزيائية والكيميائية. العلاقة الخطية لمنحني المعايرة لايون الكادميوم (II) تمتد من 0.05-12 مللي مول. لتر⁻¹ بمعامل ارتباط $r = 0.9951$. حدود الكشف كانت = 25.29 نانوغم / انموذج من التخفيف التدريجي لاقول تركيز في منحني المعايرة مع انحراف قياسي نسبي منوي RSD% اقل من 1.5 % لتركيز 8 مللي مول. لتر⁻¹ (n=5) من ايون الكادميوم (II). طبقت الطريقة بنجاح لتقدير ايون الكادميوم (II) في ثلاث نماذج لمياه النهر. اجريت مقارنة بين الطريقة المستحدثة للتحليل والطريقة التقليدية لقياس التعكسية باستخدام منحني الاضافات القياسية وبوساطة المعالجة بتحليل المتغيرات (ANOVA). لوحظ انه يوجد فرق جوهري بين الطريقتين عند مستوى قناعة 95% , حيث تم الحصول على $sig > 0.05$. على هذا الاساس بالامكان قبول الطريقة الجديدة كطريقة تحليلية بديلة.

Introduction:

Cadmium is a trace heavy metal of great importance in environmental protection. It is a highly toxic element and can be present in some coastal waters as a contaminant originating from industrial or urban waste pollution. Typical levels of cadmium in unpolluted seawater are $<0.01-9.4 \mu\text{g L}^{-1}$ [1].

Cadmium is widely used in industrial processes such as electroplating of metals, colouring agents and rechargeable Cd-Ni batteries. Cadmium is therefore found in air, water, or in plants as a result of anthropogenic pollution mainly from the smelting and refining of nonferrous metals, fossil fuel combustion and municipal waste incineration [2]. Some environmental toxic substances, such as cadmium, have a biological half-life of more than 10 years once accumulated in human body. Depending upon the route of exposure, high cadmium level can damage the kidney or lung [3,4].

literature survey reveals that various analytical methods have been reported for determination of cadmium which include FIA spectrophotometric for the determination of cadmium with detection limit of $7.6 \mu\text{g L}^{-1}$ in environmental samples[5]. Flow injection-electrochemical hydride generation (FI-ECHG) the detection limit of 0.51 ng ml^{-1} in tap water sample was obtained [6].

Sequential injection monosegmented flow analysis(SI-MSFA) with anodic stripping (AVS) detection has been developed for the determination of Cd(II) and Pb(II) with detection limit of $1.4-6.9 \mu\text{g L}^{-1}$ and applied for analysis of water sample[7].On-line preconcentration and anodic stripping voltammetry(AVS) controlled by a sequential injection analysis (SIA) for determination of lead Pb(II) and Cd(II) with detection limit of $0.01 \mu\text{g L}^{-1}$ applied for determination Cd(II) in drinking water,pond water,tap water green tea,soup,fish,cockles[8].

The working electrode of screen printed electrode sensor SPEs was constituted by a carbon film modified with Nafion with detection limit of $0.79 \mu\text{g L}^{-1}$ applied in natural water samples[9]. Graphite furnace atomic absorption spectroscopy (GF-AAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) with detection limit of $1.95 \mu\text{g L}^{-1}$ to detect cadmium in environmental and food samples[10].A flow injection analysis-flame atomic absorption spectrometric (FI-AAS) was used with detection limit of 6 ng L^{-1} of determination cadmium in sea water[11].

Flow injection preconcentration system with detection limit of 1.038 and $0.57 \mu\text{g L}^{-1}$ for 60 s and 120 s respectively, was employed for the determination of Cd(II) in industrial effluents[12].Immunoassays such as enzyme-linked immunosorbent assay (ELISA) have recently emerged as an alternative to the traditional methods, because they are usually less time-consuming, inexpensive, simple, specific and reasonably portable[13,14]. Moreover, immunoassays are able to analyze many samples simultaneously [15, 16]. Meanwhile, there is a rapidly growing interest in research related to the development of optical sensors based on chromogenic and fluorogenic reagents. Different review papers relate the developed optical systems for monitoring heavy metal ions in various matrices, with their limitations in terms of selectivity, limits of detection and reversibility[17,18].

The present work is concerned with the determination of cadmium (II) with the aid of AYA 6SX1-T-2D Solar-CFI analyzer. The method is based upon the precipitation of cadmium (II) by potassium hexacyano ferrate (III) in an aqueous medium to form a yellowish white precipitate particles from $\text{Cd}_3[\text{Fe}(\text{CN})_6]$. Turbidity was measured via the reflection of incident light from the surfaces of precipitated particles at $0-180^\circ$. The positive signal from reflection can be recorded by Ayah 6SX1-T-2D. Solar supplier with linear array of six super snow white light emitting diode as a source and two solar cell as a detector.

Experimental

Reagents and chemicals

All chemicals were used of analytical-reagent grade while distilled water was used to prepare the solutions. A standard solution (0.2 mol.L^{-1}) of cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($308.47 \text{ g. mol}^{-1}$, BDH) was prepared by dissolving 15.4235 g in 250 ml distilled water. A stock solution (0.2 mol.L^{-1}) of potassium hexacyanoferrate(III) ($\text{K}_3[\text{Fe}(\text{CN})_6]$, ($329.26 \text{ g. mol}^{-1}$, Fluka. Garanite) was prepared by dissolving 32.926 g in 500 ml of distilled water. A 1M of sulfuric acid solution (96%, 1.84 g.ml^{-1} , BDH) was prepared by pipetting 14 mL of concentrated sulfuric acid and dilute to mark with distilled water in 250 mL volumetric flask. A 1 M of hydrochloric acid solution (35%, 1.19 g.ml^{-1} , BDH) were prepared by pipetting 21 mL of concentrated hydrochloric acid and completed of the volume with distilled water in 250 mL volumetric flask. A 1 M of nitric acid solution (70%, 1.42 g.ml^{-1} , BDH) was prepared by pipetting 16 mL of concentrated Nitric acid and completed the volume with distilled water into 250 mL-volumetric flask. Each acid was standardized against standard solution of 0.1 M from NaOH

Sample preparation

500 mL of three randomly selected of geographical locations (Baghdad university , Rathwaniaya and Dura regions), were concentrated by heating followed by filtration to remove any undissolved residue affecting the response. The volumes were completed to 100 mL. 5 mL of each sample was transferred to 25 mL volumetric flask and prepared a series of solutions for standard additions curve.

Apparatus

Peristaltic pump – 2 channels (France) an Miniplus 2 type GILSON and a rotary 6-port injection valve (Teflon), (IDEX corporation, USA) was used. The response was measured by a homemade Ayah 6SX1-T-2D Solar-CFI analyzer, which uses six snow white LED for irradiation of the flow cell at 2mm path length. Two solar cell used as a detector for collecting signals via sample travel for 60 mm length. The readout of the system composed of x-t potentiometric recorder (Kompenso Graph C-1032) Siemens (Germany) or digital AVO-meter (auto range) (0-2 volt) (China). Turbidometric readings under batch conditions were made by Hanna company (U.S.A) . The flow diagram for the determination of cadmium (II) is shown in figure 1.

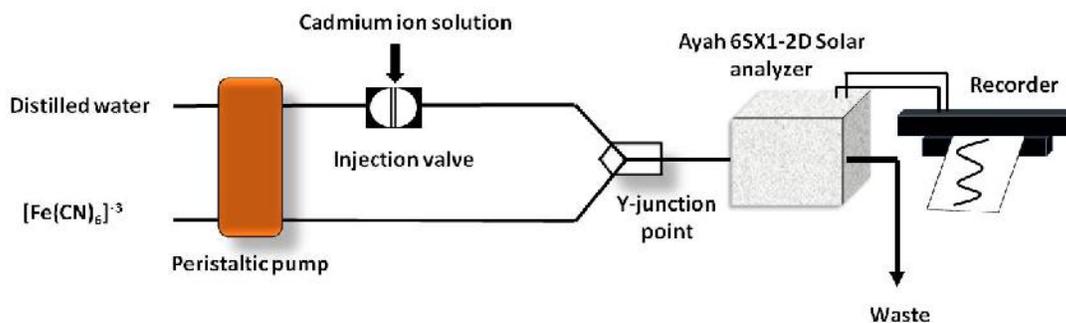


Figure.1- Flow diagram manifold system used for determination of Cd(II)

Methodology

The flow diagram shown in figure 1, for the determination of cadmium (II) by the reaction between with potassium hexacyanoferrate(III) in aqueous medium to form yellowish white precipitate for the complex $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ is composed of two lines. The first line is the carrier stream (distilled water) at 1.6 ml.min^{-1} flow rate which leads to the injection valve to carry Cd (II) sample, $45 \mu\text{l}$; while the second line supplied $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution (10 mmol.L^{-1}) at 1.6 ml.min^{-1} . Both of line meet at a junction (Y-junction), with an outlet for reactants product from $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ complex, which passes through a homemade Ayah 6SX1-T-2D Solar-CFI analyser that works with a six snow white light emitting diode was used as a source. Each solution injected was assayed in triplicate from which the response of which was recorded on x-t potentiometric recorder to measure the turbidity via the reflection of incident light that collid's on the surfaces of precipitated particles at $0-180^\circ$.

Results and Discussion

Study of the optimum parameters

The flow injection manifold shown in figure-1 was employed in the relation of chemical and physical variables, in order to obtain the optimum conditions for the system. These variables were optimized by making all variables constant and varying one each at time.

Chemical variables

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

Using variable concentration of potassium hexacyanoferrate (III) 5-150 $mmol.L^{-1}$, a constant concentration of Cd(II) 8 $mmol.L^{-1}$ with sample volume 100 μL at 1.6 $ml.min^{-1}$ flow rate and the intensity of incident light of LED 1400 mV were used to establish the optimum $K_3[Fe(CN)_6]$ concentration that can be used to formation a precipitate of $Cd_3[Fe(CN)_6]_2$. Table 1 summarizes the results obtained and figure 2 (A,B) shows that 10 $mmol.L^{-1}$ of $K_3[Fe(CN)_6]$ is the optimum concentration. An increase in concentration leads to an increase in precipitate particulates and its compactness, thus leading to a decrease in reflecting surface, therefore; this causes a decrease in peak height resulting from the reflecting light.

Table.1-Effect of $K_3[Fe(CN)_6]$ on the measurement of reflection of incident light for the determination of Cd(II).

$[Fe(CN)_6]$ $mmol.L^{-1}$	Reflection of incident light expressed as Average peak height (n=3) in (mV)	RSD%	Confidence interval at (95%) $\bar{y} \pm t_{0.05/2} \sigma_{n-1} / \sqrt{n}$
5	1410	0.709	1410 \pm 24.873
10	1453.33	0.795	1453.30 \pm 28.721
50	1352.67	0.814	1352.67 \pm 27.398
100	1206.67	0.957	1206.67 \pm 28.721
150	1110.67	0.906	1110.67 \pm 25.038

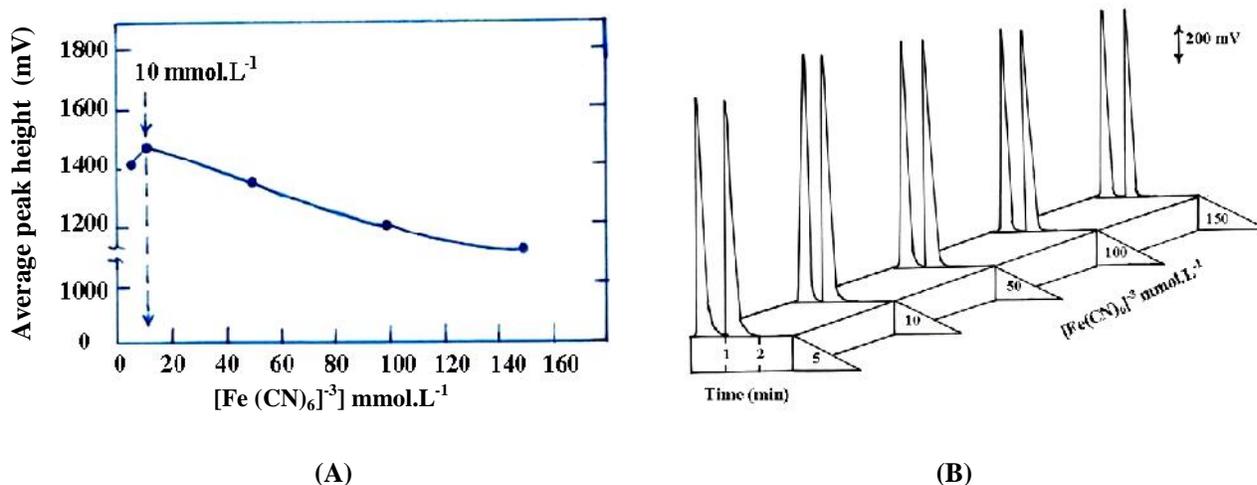


Figure 2- Effect of the $K_3[Fe(CN)_6]$ on (A) Energy transducer response by reflection of incident light
(B) Response profile

Effect of acidic media on the increase of incident light intensity

The precipitation of Cd(II) by $K_3[Fe(CN)_6]$ was studied in different acidic media (Sulphuric acid, hydrochloric acid and nitric acid) at 50 $mmol.L^{-1}$ concentration in addition to the aqueous medium yielding immediately a yellowish white precipitate of $Cd_3[Fe(CN)_6]_2$ complex. Figure 3 shows the variation of transducer energy response express as average peak height (n=3) in mv with different media. It can be seen that a high response in aqueous medium as a carrier stream was obtained

compared with the use of different acids. This is most probably attributed to the decrease in the amount of precipitate due to the relative solubility in acidic medium. Therefore; water was chosen as the optimum medium to obtain a maximum response.

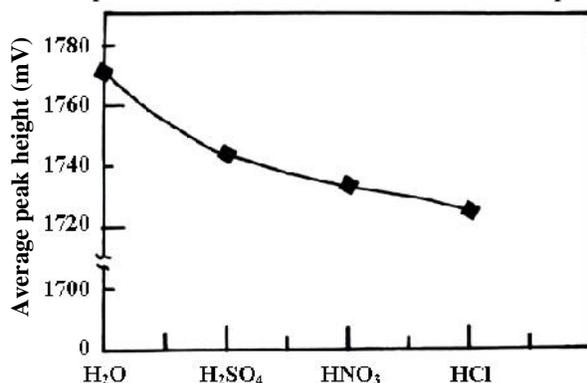


Figure.3-Effect of the acidic media & water on the reflection of light [condition: Cd(II)(10 mmol.L⁻¹), K₃[Fe(CN)₆](10 mmol.L⁻¹), 100μl & flow rate 1.6 ml.min⁻¹].

Physical variables

Flow rate Effect of

Using optimum concentration of the reactant, K₃[Fe(CN)₆] 10 mmol.L⁻¹, concentration 10 mmol.L⁻¹ of Cd(II) and sample volume 100 μl with a variable range 0.8 to 2 ml.min⁻¹ flow rate for the carrier stream and K₃[Fe(CN)₆] solution line were studied. Figure 4 (A, B) shows that the best flow rate for the completion of the precipitate of Cd(II) by K₃[Fe(CN)₆] is 1.6 mL.min⁻¹ for both of lines in flow injection system figure.1. The results obtained were summarized in table 2. It was noticed at slow flow rate, there is increase in dilution and dispersion which might be caused an increase in base width t_B of response, while at higher flow rate (>1.6 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 not very high due to settling rate of precipitate particulates from measuring cell prior to completion of reaction. Therefore; a flow rate of 1.6 ml.min⁻¹ was adopted for Cd(II) determination to obtain a maximum response and less t_B as shown in figure 4(A,B).

Table 2- Effect of the variation of flow rate on the measurement of reflection of incident light.

Flow rate ml.min ⁻¹	Reflection of incident light expressed as Average peak height (n=3) in (mV)	RSD%	Confidence interval at (95%) $\bar{y} \pm t_{0.05/2} \sigma_{n-1} / \sqrt{n}$	Base width Δt_B (sec)	t Arrival time to the measuring cell (sec)
0.8	1192	0.089	1192±26.322	90	90
1	1340.67	0.086	1340.67±2.872	84	39
1.2	1550	0.645	1550±24.873	81	30
1.4	1558.33	0.490	1558.33±18.997	78	24
1.6	1579.33	0.073	1579.33±2.872	48	21
1.8	1551.67	0.671	1551.67±25.888	45	12
2	1513.33	0.763	1513.33±28.721	30	11

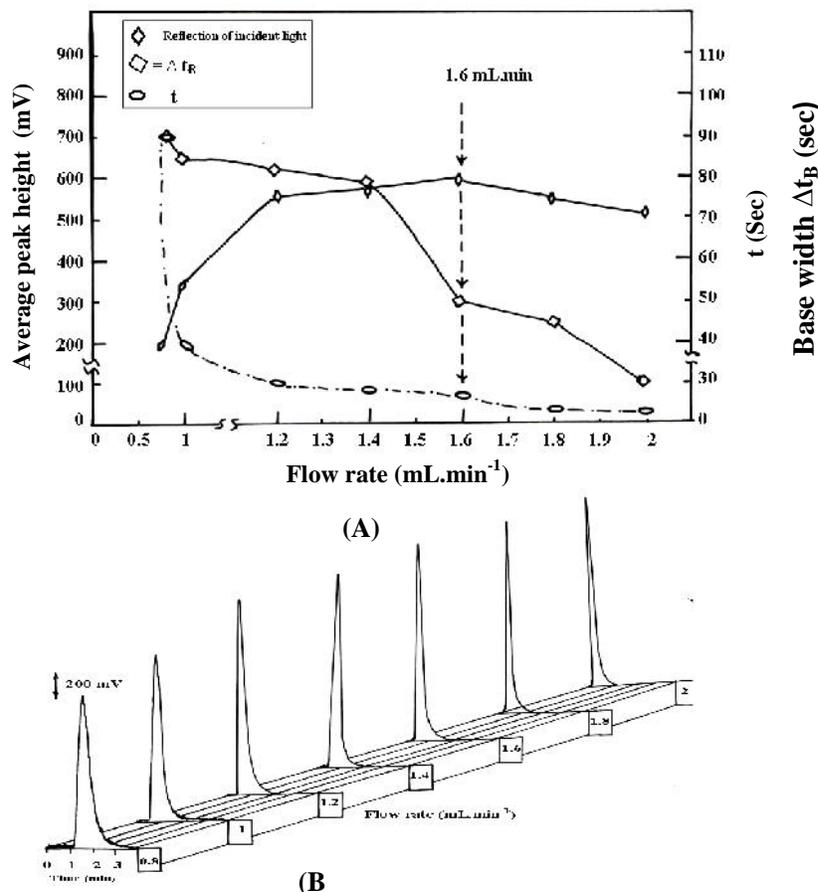


Figure .4 Effect of the variation of the flow rate on the

A- Transducer energy response expressed as peak height in mV for Reflection of incident light for Cd(II) (10 mmol.L^{-1}) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (10 mmol.L^{-1}) $100\mu\text{l}$, flow rate 1.6 mL.min^{-1}

B- Response profile

Effect of sample volume

Using the optimum flow rate of 1.6 mL.min^{-1} with a various volumes ($26\text{-}200\mu\text{l}$) by changing the length of sample loop in the injection valve were injected using open valve mode i.e. allowance for continuous purge of sample from the sample loop in the injection valve. table 3 shows the injected sample volume, each was repeated three times successively. The data obtained were plotted as depicted in figure 5(A,B), showing that the optimum sample volume is $45 \mu\text{l}$ gave a regular response. The increase of sample segment (more than $45 \mu\text{l}$) 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 the loss of some of the reflecting surface otherwise the will be available to reflect incident light. Due to this probable explanation, the peak profile i.e response versus time will be broad as shown in figure 5(A, B).

Table 3-Effect of the variation of sample volume on the measurement of reflection of incident light for determination Of: Cd(II)(10 mmol.L⁻¹), K₃[Fe(CN)₆] (10 mmol.L⁻¹) & flow rate 1.6 ml.min⁻¹.

Sample volume μl	Reflection of incident light expressed as Average peak height (n=3) in (mV)	RSD%	Confidence interval at (95%) $\bar{y} \pm t_{0.05/2, n-1} / \sqrt{n}$	Base width t_B (sec)	t Arrival time to the measuring cell (sec)
26	1306.67	0.442	1306.67 \pm 14.360	66	9
45	1748.33	0.165	1748.33 \pm 7.180	69	10.8
100	1645	0.304	1645 \pm 12.436	90	12
140	1915	0.261	1915 \pm 12.436	99	15
200	1991.67	0.383	1991.67 \pm 18.997	108	18

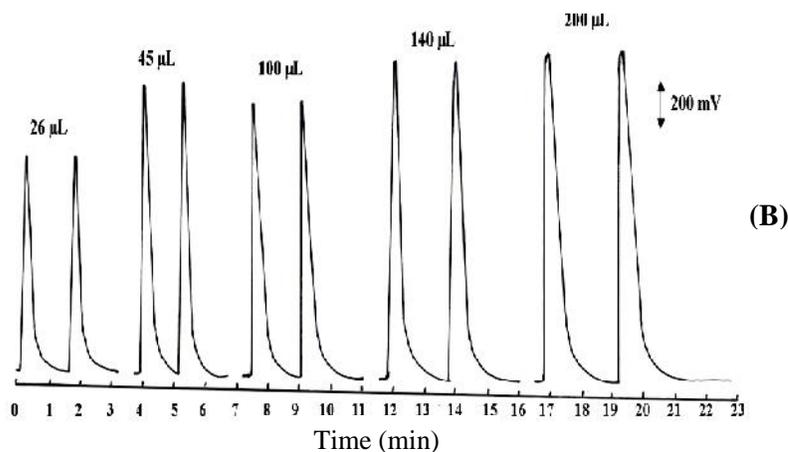
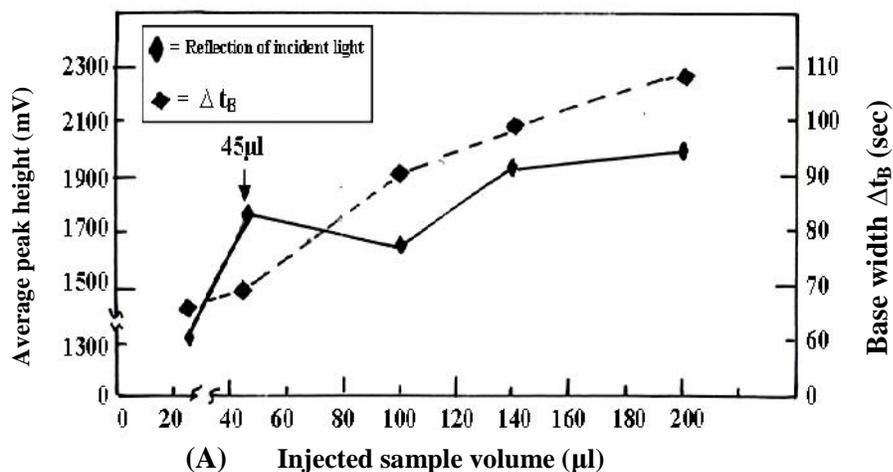


Figure 5 Effect of the variation of sample volume on the
 A- Transducer energy response expressed as peak height in mV for reflection of incident light for Cd(II)(10 mmol.L⁻¹), K₃[Fe(CN)₆](10 mol.L⁻¹) and flow rate 1.6 mL.min⁻¹
 B- Response profile

Effect of purge time

Different purge times for the sample segment of 2-20 seconds were used for this study in addition to allow the injection valve in the open mode. Time for the carrier solution to pass through the injection valve in injection mode followed by turning the injection valve to the load position. Sample volume 45 μl was used with concentration of Cd(II) of 10 mmol.L⁻¹. figure 6(A,B) shows the continuation of the

increase in transducer energy response with increase of injection time up to 10 seconds followed by a relatively constant in a height of responses. Therefore; 10 seconds a purge time was chosen as optimum time to the complete purge of the sample from sample loop.

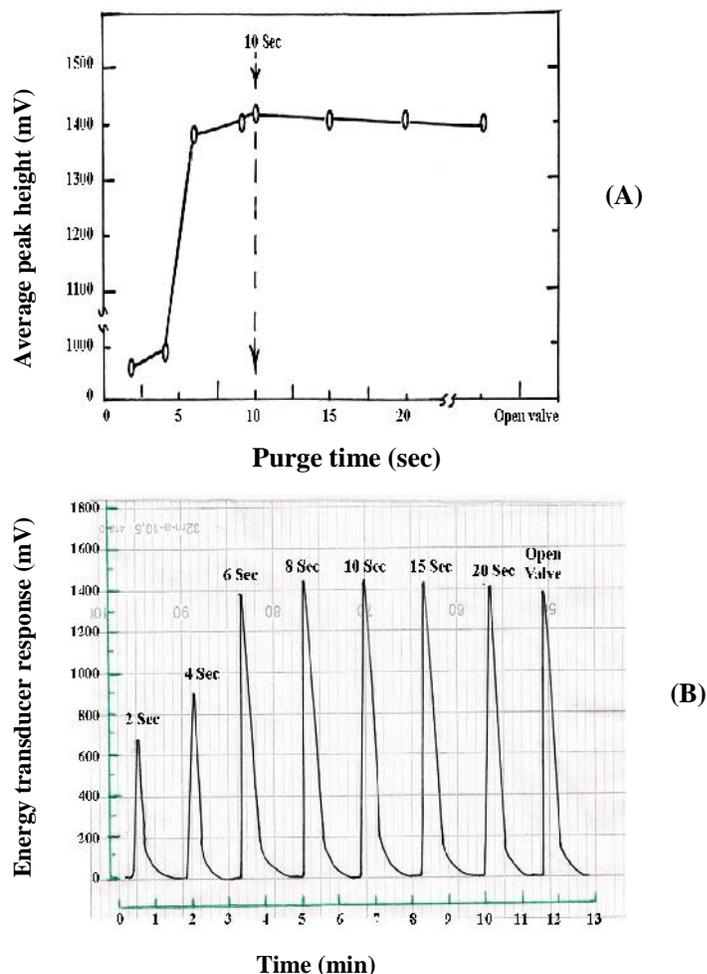


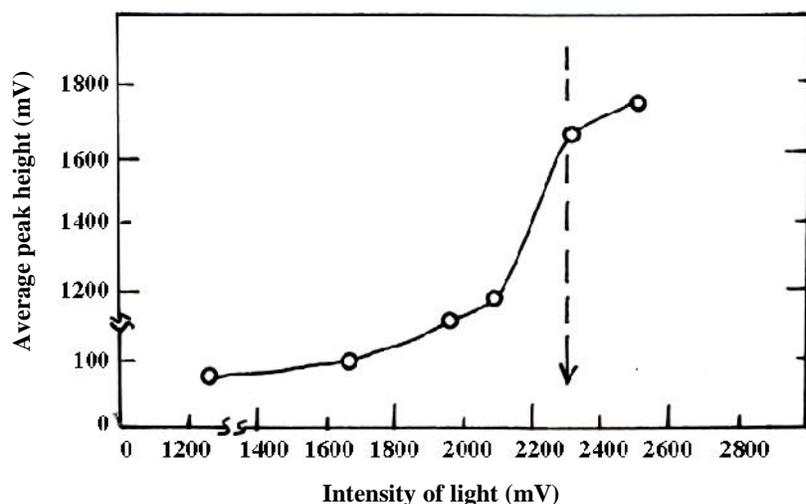
Figure 6-Effect of the variation of purge time on the
A- Transducer energy response expressed as peak height in mV for Reflection of incident light for Cd(II)(10 mmol.L⁻¹),K₃[Fe(CN)₆] (10 mmol.L⁻¹) 45μl & flow rate 1.6 ml.min⁻¹
B- Response profile

Effect of incident light intensity

Intensity of light source was studied using the optimum physical and chemical parameters achieved in previous sections, with 10 mmol.L⁻¹ Cd(II). Variable intensity of light source was used 1.36-2.5 volt by variation of light intensity channel in Ayah 6SX1-T-2D Solar CFI Analyser operation where read by AVO-meter. The results tabulated in table 4 which shows that an increase on the reflection of incident light by precipitate particles of Cd₃[Fe(CN)₆]₂ with increased intensity of source light. The intensity of 2.31 volt was selected as the optimum voltage that can be supplied to give a better transducer energy response as shown in figure.7.

Table. 4 -Effect of intensity of light on the measurement of reflection of incident light expressed as transducer energy response

Intensity of light (mV)	Reflection of incident light expressed as Average peak height (n=3) in (mV)	R.S.D%	Confidence interval at (95%) $\bar{y} \pm t_{0.05/2} \sigma_{n-1} / \sqrt{n}$
1360	703.33	0.821	703.33±14.360
1680	906.67	0.842	906.67±18.997
1960	1112	0.238	1112±6.581
2080	1173.33	0.984	1173.33±28.721
2310	1635	0.306	1635±12.436
2500	1745	0.287	1745±12.436

**Figure .7**-Effect of the variation of light intensity on the reflection of light expressed as a positive transducer energy response in (mV) for Cd(II)(10 mmol.L⁻¹), K₃[Fe(CN)₆] (10 mmol.L⁻¹), 45μl & flow rate 1.6 ml.min⁻¹.**Calibration graph for Cd(II)**

A series of Cd(II) solutions ranging from 0.05 to 15 mmol.L⁻¹ were prepared and injected at the established optimum condition. A scatter plot diagram was constructed between the variation of the energy transducer responses versus concentration of Cd(II) showing a linear dynamic range from 0.05 to 12 mmol.L⁻¹. Figure 8 shows the calibration graph using simple linear equation of form $y = a+bx$ table 5 displays the correlation coefficient, linear percentage, straight line equation and the calculated t-value at 95% confidence of 34.70 which larger than tabulated t-value indicating clearly that the linearity against non-linearity is accepted.

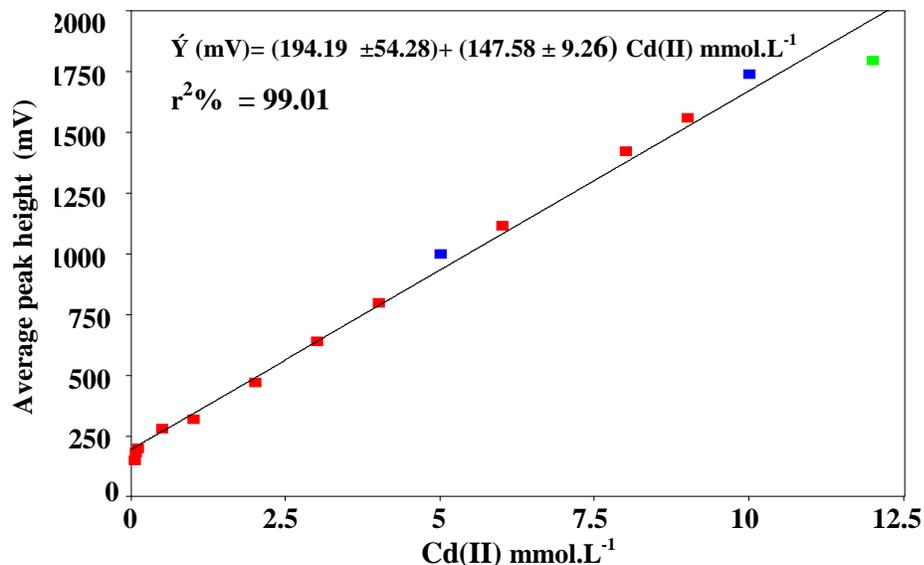


Figure8-Calibration graph of Cd(II) concentration.

Table 5-Summary of linear regression [19, 20] for the variation of energy transducer response with Cd(II) concentration using simple regression line of the form $(\hat{Y} = a + bx)$ at optimum conditions.

Concentration measured mmol.L ⁻¹	Concentration range mmol.L ⁻¹ n=14	$(\hat{mV}) = a \pm s_a + b \pm s_b t[x]$ At confidence interval 95%, n-2	r r ² %	t _{tab} at 95%, (n-2)	Calculated t-value $\frac{t/r}{\sqrt{1-r^2}}$
0.05-15	0.05-12	194.19±54.28+147.58±9.26[x]	0.9951 99.01	2.179	<34.70

\hat{Y} = Estimated response (mv) for (n=3), [x] = Cd(II) con.(mmol.L⁻¹), r=correlation coefficient, r²%;linearity percentage

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 6 tabulates all these calculated values of detection limit for 45 µL sample solution.

Table.6-limit of detection for Cd(II) at optimum parameters in different approaches

Practically Based on the gradual dilution for the minimum concentration	Theoretical based on the value of slope $x = 3s_B/\text{slope}$	Based on the linear equation $\hat{Y} = Y_B + 3s_B$
25.29 ng/sample	39.10 ng/sample	6.43 µg/sample

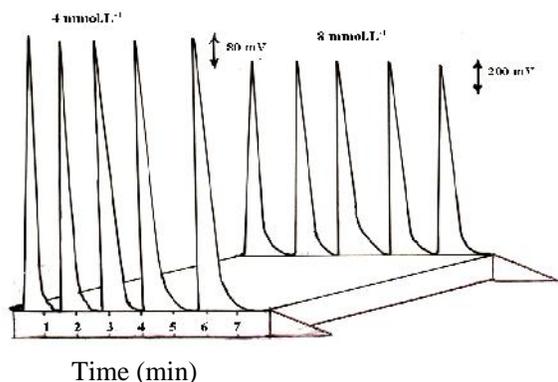
X= value of L.O.D based on slope, S_B=standard deviation of blank repeated for 13 times, Y_B=Average response for blank= intercept, L.O.D=limit of detection

Repeatability

The repeatability of measurement and the efficiency of homemade Ayah 6SX1-T-2D Solar CFI analyser were studied at fixed concentrations of Cd (II) with two concentrations at 4 and 8 mmol.L⁻¹ using the optimum parameters. A repeated measurements for five successive injections were measured and obtained results are tabulated in table 7 which shows that the percentage relative standard deviation was less than 1%. Figure 9 shows a kind of response-time profile for the used concentrations

Table 7-The repeatability test.

Cd(II) mmol.L ⁻¹	Average response	RSD %	$\bar{y} \pm t_{0.05/2, n-1} / \sqrt{n}$ At confidence interval 95%	Number Of injection
4	793	0.564	793±11.123	5
8	1424	0.294	1425±10.406	5

**Figure 9-**Response-time of five successive repeatable measurements of cadmium(II) concentration (4,8 mmol.L⁻¹).**Calibration graph of Classical method**

Calibration graph of classical method (measurement of turbidity by HANNA instrument) was made to the determination of Cd(II) from 0.05-15 mmol.L⁻¹ after fixing the optimum $[\text{Fe}(\text{CN})_6]^{3-}$ which was 10 mmol.L⁻¹. Table 8 tabulates all the obtained data for the classical method, while table 9 shows the comparison of both methods. The results indicated that the proposed method was more sensitive than the classical method.

Table 8- Summary of linear regression for determination of Cd(II) by Cd(II) – $[\text{Fe}(\text{CN})_6]^{3-}$ system using classical method .

Concentration measured (mmol.L ⁻¹)	Concentration range mmol.L ⁻¹ (n=14)	$(mV) = a \pm s_a t + b \pm s_b t [x]$ At confidence interval 95%, n-2	r r ² %	t_{tab} at 95 % (n-2)	Calculated t-value $\frac{t}{r / \sqrt{n-2}}$ $\sqrt{1-r^2}$	LOD Practically Based on the gradual dilution for the minimum concentration
0.05-15	0.05-7	$36.12 \pm 24.20 + 91.13 \pm 7.88 [x]$	0.9954 99.07	2.365	$2.365 \ll 27.364$	28.10 µg/Sample

Table 9- Summary of result compared between Classical method & present method

Analytical parameter	Classical method	Ayah 6SX1-T-2D solar analyzer FIA
r ² %: linearity percentage	99.07	99.01
Linear range mmol.L ⁻¹	0.05-7	0.05-12
Sensitivity (b)	91.25 FTU/mmol.L ⁻¹	147.58 mV/mmol.L ⁻¹
Intercept (a)	36.12 FTU	194.19 mV
Limit detection practically	28.10 µg/Sample	25.29 ng/sample
Sample volume	10 ml	45 µl
Repeatability (n=5)RSD%	5.25	< 1%

FTU: Formazine turbidity unit

Application

Two methods were used to the determination cadmium ion in a random river samples from Baghdad suburb. The methods were firstly using Ayah 6SX1-T-2D Solar CFI analyser while the second method was to used the classical measurement for turbidity. A series of solution were prepared of each sample by transferring 5 mL to each of the five volumetric flask (25 ml), followed by the addition of 0, 1.25, 7.5, 12.5, 17.5 mL from 10 mmol.L⁻¹ standard solution of Cd(II) in order to have the concentration range from (0-7) mmol.L⁻¹. Flask no.1 is the sample volume. table 10 shows the summary of standard additions method results from the three samples with the amount of Cd(II) in water samples. table 11 shows the two-way ANOVA to test the effects of the two methods used for analysis and the kind of water samples supplied from different geographical locations. Colume no.6. showed that the sig<0.05,indicated that there was a significant difference between two methods and water samples for 95% confidence level.

Table 10- Results for determination of Cd(II) in real sample by two method using standard addition

Type of Sample	Equation of standard additions curve at 95%,n-2 $mV=a+ b [x]$	r $r^2\%$	Cd(II) mmol.L ⁻¹ In 25 mL In 100 mL Sample	t_{tab} at 95 % , n-2)(Calculated t-value $\frac{t/\sqrt{n-2}}{\sqrt{1-r^2}}$
	AYAH 6SX1-2D Solar CFIA				
	HANNA instrument (classical method turbidity measurement)				
University of Baghdad	86.65 + 110.11 [X]	0.9980 99.61 %	0.8 mM 4 mM		3.182<<27.68
	52.30 + 60.09 [X]	0.9590 91.99%	0.9 mM 4.5mM		3.182<<5.86
Alratuania	180.37 + 132.78 [x]	0.9943 98.88	1.36 mM 6.79 mM		3.182<<16.25
	96.46 + 66.24 [x]	0.9682 93.75%	1.46 mM 7.28 mM		3.182<<6.71
Al-Dura	268.64 + 160.89 [x]	0.9967 99.34%	1.7 mM 8.5 mM		3.182<<24.63
	156.39 + 87.42 [x]	0.9898 97.96%	1.8 mM 9 mM		3.182<<12.02

Table 11- Summary of two-way (ANOVA)

Source	Sum of squares (SS)	Df	Mean square MS=SS/Df	F MSS/Err	p	Inference
Corrected model	0.804	2	0.402	32.63	0.009	Sig<0.05 Difference significant
Location	0.202	1	0.202	16.434	0.027	Sig<0.05 Difference significant
Method	0.602	1	0.602	48.83	0.006	Sig<0.05 Difference significant
Error	0.037	3	0.012			
Corrected total	0.841	5				

ANOVA: Analysis of variance

Conclusion

The proposed FIA method is simple, rapid, sensitive, inexpensive and exhibits a fair degree of precision and accuracy. The method does not involve any critical reaction conditions and can be compared favorably with other existing methods. The proposed method can serve as an alternative method for the determination of Cd(II) in water samples.

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