New Approach for the On-Line Spectrophotometric Determination of Vanadium (V) 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 new simple sensitive and selective spectrophotometric method has been developed for the analysis of vanadium(V) in three randomly chosen samples from river water at different locations by continuous flow injection analysis. The method based on the oxidation of pyrogallol by vanadium(V) in acidic solution to form color species and the same species was determined using homemade Ayah 6SX1-T-2D solar cell analyser . Chemical and physical parameters were investigated using the high intensity of snow white light emitted diode as a source. The linear dynamic range for the instrument response versus vanadium(V) concentration was 1-200 mg.L^{-1} with correlation coefficient r = 0.9920. The limit of detection (S/N=3) was 70 ng/ sample from the step wise dilution for the minimum concentration in the linear dynamic range of the calibration graph with RSD % of lower than 1% at 90 mg.L^{-1} (n=5) concentration of vanadium(V). The method was applied successfully for the determination of vanadium (V) in three river samples. A comparison was made between: both of the proposed methods and classical method (UV-Vis spectrophotometry at wave length 427 nm)   using the standard additions method via the use of paired t-test. It was noticed that there was no significant difference between two methods at 95 % confidence level.

Keywords: Vanadium (V),spectrophotometry, Flow injection analysis

نمط جديد للتقدير الأني الطيفي لأيون الفناديوم في مختلف مياه الانهار من خلال محلل جديد مصنع محليا للحقن الجرياني المستمر (Ayah 6SX1-T-2D Solar).

نغم شاكر تركي العوادي*، عمر اياد ياسين

قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

طورت طريقة تحليلية جديدة ، بسيطة، وانتقائية لتقدير ايون الفناديوم في المحاليل المائية لثلاث نماذج عشوائية الاختيار من مياه الانهار ولمواقع مختلفة عن طريق اكسده البايروكالول بفناديوم(V) في الوسط الحامضية لتكوين اصناف ملونة والتي قدرت باستخدام محلل الحقن الجرياني المستمر Ayah 6SX1-T- 2D Solar المصنع محلياً. تم دراسة كافة المتغيرات الفيزيائية والكيميائية باستخدام شده عالية من ثنائي وصلة باعث للضوء الابيض الثلجي كمصدر. المدى الخطي لعلاقة تغير الاستجابة الالية مع تركيز الفناديوم (V) (200–1) ملي غم.مل$^{-1}$ بمعامل ارتباط r=0.9920. حدود الكشف (S/N=3) (3SB=) 70

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نانوغم/انموذج من التخفيف التدريجي لاقل تركيز في منحي المعايرة مع انحراف قياسي نسبي RSD%

للتكرارية اقل من 1% لتركيز 90 ملي غم.لتر$^{-1}$ (n=5) من الفناديوم (V). طبقت الطريقة بنجاح لتقدير ايون

الفناديوم(V) في ثلاث نماذج لمياه النهر . اجريت المقارنه بين الطريقتين (الطريقة المقترحه والطريقة التقليدية

للقياس الطيفي عند λmax= 427 نانومتر) باستخدام منحني الاضافات القياسية عند اختبار t–المزدوج .

لوحظ انه لايوجد فرق جوهري بين الطريقتين عند مستوى قناعة 95%.

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Introduction

   Vanadium is a highly distributed in the Earth's crust but it is never found unbound in nature. Vanadium occurs in about 65 different minerals and in carbon-containing deposits such as crude oil, coal, oil shale, and tar sands. Watering is an important way in which vanadium is redistributed throughout the environment because venedates are generally very soluble. Vanadium is present in natural water in concentrations ranging between 1×10^{-7} and 5×10^{-7} mol L^{-1} [1,2].Vanadium is important, particularly from a biological and industrial point of view. It is a metallic element that occurs in six oxidation states in numerous inorganic compounds. It is used primarily as an alloying agent in steels and non-ferrous alloys. Vanadium compounds are also used as catalysts and in chemical, ceramic or specialty applications. Also, in-vitro studies have shown that vanadium is essential for cell growth at μg dm^{-3} levels, but can be toxic at higher concentrations. The toxicity of vanadium depends on its physico-chemical state; particularly on its valance state and solubility [3,4]. In body, vanadium can undergo changes in oxidation state (V (V) and V (IV) forms) and it can also bind with blood protein. V (IV) is less toxic than V (V) in environmental systems and can be produced by various industrial redox processes. It was observed that V (IV) in aqueous solutions forms complexes, most easily with reagents containing oxygen or sulfur donor ligands[5-7] literature survey reveals that various analytical methods have been reported for determination of vanadium which include emission spectroscopy [8], neutron activation analysis[9,10] inductively coupled plasma atomic emission spectrometry (ICP-AES)[11-13]spectrophotometry[14-16] amberlite XAD resin[17]silica gel[18,19] capillary electrophorsis (CE)[20] ion chromatography[21]. Chemiluminescence[22,23]**.**

This work describes a flow injection spectrophotometric method for determination of vanadium (V) with the aid of Ayah 6SX1-T-2D Solar-CFI analyser in river waters. The method is based upon the oxidation of pyrogallol by vanadium(V) in acidic medium to forms a red-yellowish color species which measured at λ_{max}= 427 nm . The procedure is simple, rapid and is proposed for the control analysis of the vanadium (V) in river waters as an alternative analytical procedure.

Experimental

Reagents and chemicals

   All chemicals were used of analytical-reagent grade while distilled water was used to prepare the solutions. A standard solution (1000 mg.L^{-1})of sodium metavanadate NaVO$_3$ (121.94 g.mol^{-1},BDH)was prepared by dissolving 0.5984 g in 250 mL of 5 % nitric acid .A stock solution (1 mol.L^{-1}) of pyrogallol C$_6$H$_6$O$_3$ (126.11 g.mol^{-1}BDH) was prepared by dissolving 31.5275 g in 250 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 250 mLvolumetric 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 the volume with distilled water in 250 mL. 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 in to 250 mL. Each acid was standardized aganist standard solution of 1 M of Na$_2$CO$_3$. A standard solution (1 mol.L^{-1}) of sodium carbonate Na$_2$CO$_3$ (106 g.mol^{-1},BDH) was prepared by dissolving 26.5 g in 250 mL of distilled water.

Sample preparation

   500mL of three randomly selected of geographical locations (Baghdad university , Rathwaniaya and Dura regions), were concentrated by heating followed by filteration to remove any undissolved residue affecting to the response. The volumes were completed to 250 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 rotary 6-port medium pressure injection valve (Teflon),(IDEX corporation, USA) used for injection of sample. The response was measured by a homemade Ayah 6SX1-T-2D Solar-CFI analyser which uses six snow white LED for irradiation of the flow cell at 2 mm 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) 200 mV,(2-100 volt) (China). UV-Vis spectrophotometer digital double beam type UV-1800, shimadzu, Japan were also used to scan the spectrum of colored species using 1cm quartize cell. The flow diagram for the determination of vanadium(V) is shown in figure 1
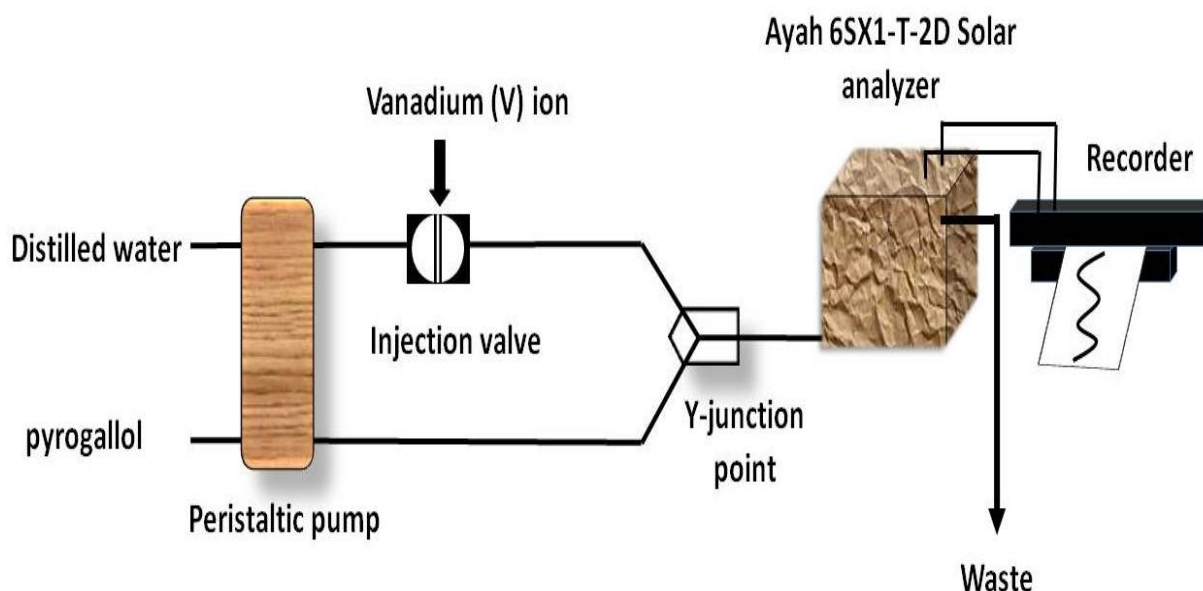

Figure1.-Flow diagram manifold system used for the determination of vanadium (V) ion

Methodology

The whole reaction manifold system for the determination of vanadium(V) ion as shown in figure-1 via directly oxidation of pyrogallol by vanadium(V) in acidic solution to form red-yellowish color species. The system is composed from two lines: the first line supplied with distilled water at 1.8 mL.min^{-1} which leads to the injection valve for carrying vanadium(V) sample with 140 μL sample volume , while the second line supplied pyrogallol solution (1 mmol.L^{-1}) at 1.8 mL.min^{-1}. Both of lines meet at junction (Y-Junction) with an outlet from which the reactants product of red-yellowish color species passes through Ayah 6SX1-T-2D-CFIA analyse works with a six snow white light emitting diode will be used as a source. Each solution injected was assayed in triplicate. The response of which was recorded on x-t potentiometric recorder to measurement the absorbance for color species. A proposed mechanism of oxidation pyrogallol by vanadium (V) ion in acidic medium[23] is presented in figure 2
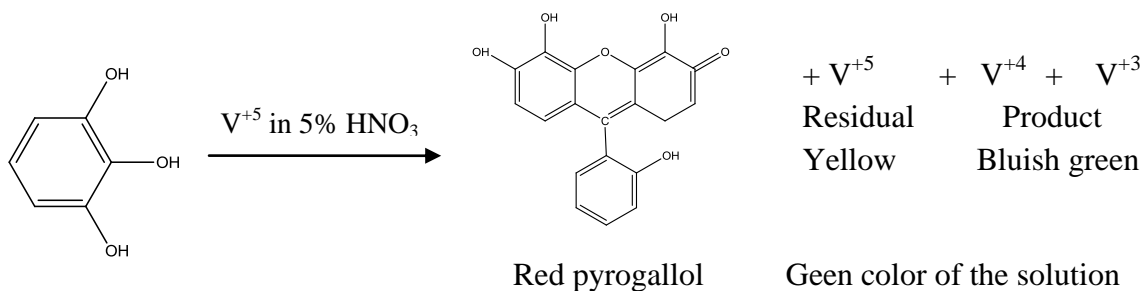

Figure.2- Mechanism for the reaction between vanadium (V) ion and pyrogallol

Results and Discussion
Scanning of spectrum for pyrogallol- vanadium(V) – H₃O⁺ system
A study were carried out to obtained λ_{max} for colored product (red-yellowish) via using the pyrogallol (50 mmol.L^{-1})-vanadium 10 mg.L^{-1} (in 5 % HNO₃) system. It can be seen that a maximum absorbance of pyrogallol at 242 nm figure- 3-A while the maximum absorbance of vanadium (V)(yellow color) in 5 % HNO₃ at 364 nm figure-3-B. Pyrogallol mixed with vanadium(V) as oxidation agent, an intense (red-yellowish) colour product was formed immediately, the product shows a maximum absorption at 427nm against reagent blank (pyrogallol,5% HNO₃) as shown in figure-3-.C.
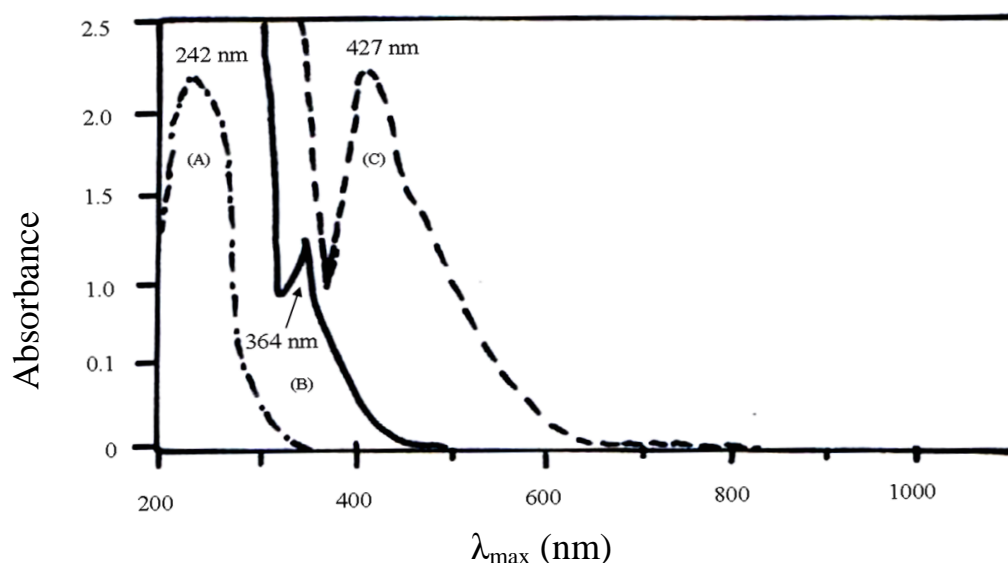

Figure 3-Absorbance spectra for : (A) pyrogallol , (B) vanadium , (C) pyrogallol-vanadium (V)- H₃O⁺ system

Study of the optimum parameters
   The flow injection manifold system as shown in figure-1 was investigated in the relation of chemical and physical variables, in order to obtained optimum conditions for the system. They were optimized by making all variables constant and varing one each at time.
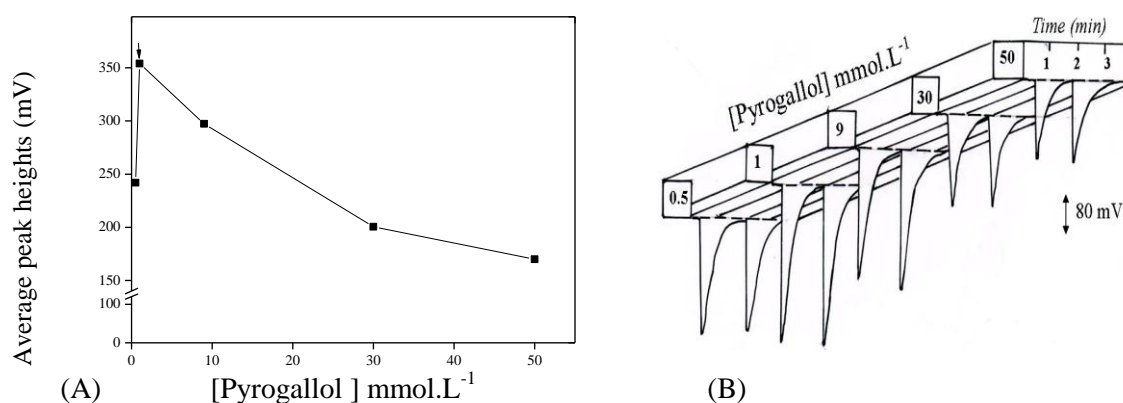
Chemical variables
Effect of pyrogallol Concentration
   Using the preliminary experiment parameters of vanadium (V) 200 mg.L^{-1}, flow rate (1.6 mL.min^{-1}) and 140 µl sample volume. A study was conducted to optimize the preferred concentration of pyrogallol in the range (0.5-50) mmol.L^{-1}. Table-1 summarizes the data obtained showing the average of the three successive readings, relative standard deviation and confidence interval of the average responses at 95% confidence ($\alpha = 0.05$). From the results obtained, it was noticed that the optimum pyrogallol concentration was 1 mmol.L^{-1}. Figure-4-A,B shows the plot of the results and responsing profile which was obtained from Ayah 6SX1-T-2D –CFI solar analyser. It was noticed an increasing of response to the height of colored species with increasing pyrogallol concentration up to 1 mmol.L^{-1}, while at higher concentration (more than 1 mmol.L^{-1}) lead to a decrease in response height, this may be due to increase of the density of the colored product which work as an internal filter that really prevent the remaining light intensity after absorption process by the colored species from passes to the solar cell detector. In addition, at high concentration mostly attributed to the formation of small colored colloidal precipitate that might be formed in front of the detector causing a distortion of the peak maximum

Table.1-Effect of pyrogallol concentration on the measurement of transducer energy response of vanadium (V)

Confidence interval at (95%) $\bar{y} \pm t_{0.05/2,n-1} \sigma_{n-1}/\sqrt{n}$	RSD%	Transducer energy response expressed as average peak heights(n=3) $\bar{y}_i$ in (mV)	[Pyrogallol] mmol.L^{-1}
242±4.975	0.826	242	0.5
354±4.975	0.565	354	1
297.33±5.744	0.777	297.33	9
200.8±1.316	0.264	200.6	30
170±3.799	0.897	170	50

Figure 4-. Effect of the pyrogallol (A)Transducer energy response expressed as average peak heights (B) Response profile

Effect of acidic media

The effect of different media on the sensitivity, in general, was studied in different acidic media (HCl,H_2SO_4 and HNO_3,) at 50 mmol.L^{-1} in addition to the aqueous medium as a carrier stream.Using the optimum concentration of pyrogallol achieved in previous section, flow rate 1.6 mL.min^{-1} with 140 µl sample volume.Table.2 summarizes the obtained results, while figure-5-A,B shows the plot of the results and response profile which was obtained from Ayah 6SX1-T-2D –CFI solar analyser. It can be seen that the distilled water as the best medium due to that the most suitable for completely the oxidation of pyrogallol by vanadium (V). while the acids such as (HNO3 and HCl) cause to decrease of output transducer energy response; mostly attributed to dissociation the color species and H2SO4 due to the precipitated a vanadium ion as form of vanadium sulphate.

Table 2- Effect of acidic media as a carrier stream on the transducer energy response for determination vanadium(V)

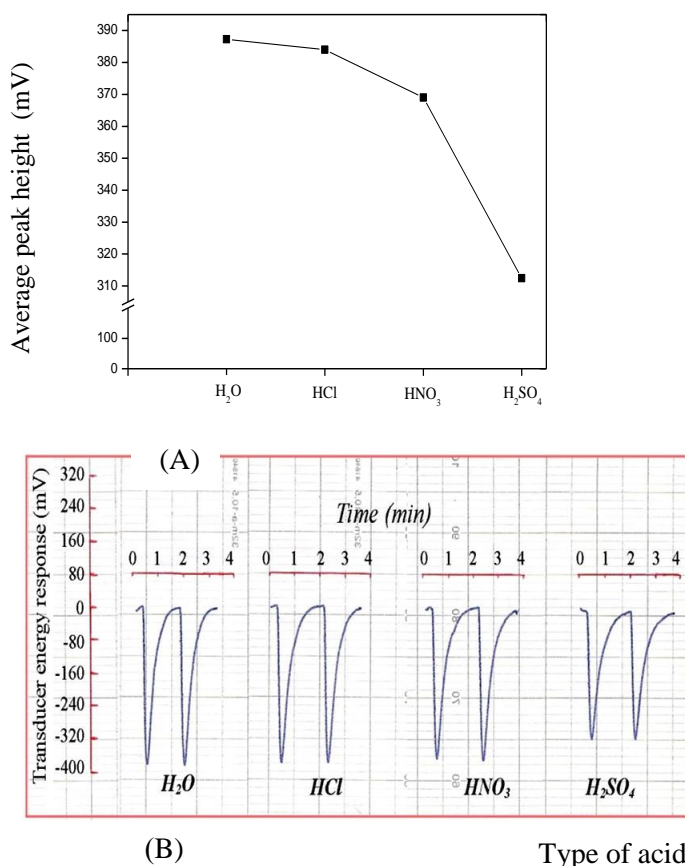| Type of acid	Transducer energy response expressed as average peak heights (n=3) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2,n-1} \sigma_{n-1}/\sqrt{n}$
H_2O	387.27	0.209	387.27±2.010
HCl	384	0.138	384±1.316
HNO_3	369	0.271	369±2.487
H_2SO_4	312.4	0.128	312.4±0.995

(A)

(B)   Type of acidic

Figure 5- Effect of the pyrogallol (A)Transducer energy response expressed as average peak heights (B) Response profile

Physical variables
flow rate Effect of

   A set of experiments were conducted for the optimization of the preferred flow rate (0.8-2 mL.min^{-1}) using the optimum concentration of pyrogallol (1 mmol.L^{-1}), 200 mg.L^{-1} of vanadium ion and 140 μl sample volume. Table-3 summarizes the obtained results including average of three successive readings, the arrival time of sample segment to the flow measuring cell (sec) and base width of response Δt_B (sec). it was noticed that at low flow rate, there were an increase in peak base width Δt_B as shown in figure-6-A,B. This might be due to the decrease of affect the physical variables (i.e dispersion and dilution on the sample segment) at the same time leading to obtain an irregular response. While at higher flow rate > 1.8 there were a decrease in the response in spite of obtaining sharp maxima as shown in figure-6-B.This might be due to the incompletion of oxidation reaction or unavailability of enough time for the response measurement before it is departure of the color segment from the measuring cell at a short time. Therefore, a flow rate of 1.8mL.min^{-1} was chosen as optimum throughout this work.

Table.3- Effect of the variation of flow rate on the transducer energy response.

Flow rate mL.min^{-1}	Transducer energy response expressed as average peak heights (n=3) $\bar{y}_i$ in(mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2,n-1} \sigma_{n-1}/\sqrt{n}$	Base width Δt_B (sec)	t* (sec)
0.8	330	0.606	330±4.975	126	33
1	343.6	0.116	343.6±0.995	114	30
1.2	357.33	0.646	357.33±5.74	102	21
1.4	377	0.265	377±2.487	84	18
1.6	386.33	0.539	386.33±5.177	81	17.4
1.8	450	0.588	450±6.581	72	12.6
2	388.13	0.465	388.13±4.486	70.8	12

   t* = Departure time for sample segment from injection valve to the measuring cell
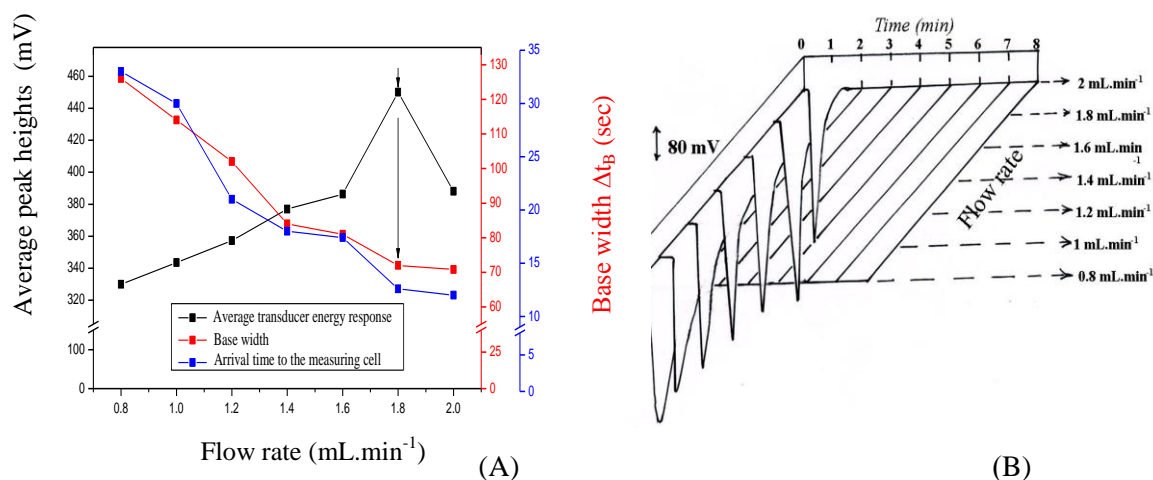
Figure 6- Effect of the variation of flow rate on the transducer energy response expressed as peak heights in mV , Base width and Arrival time to the measuring cell. B- Response profile

Effect of sample volume

Using the optimum parameters of flow rate(1.8ml.min^{-1}) and pyrogallol 1mmol.L^{-1} for the determination of vanadium (V). Variable sample volumes (26, 45, 100,,140 and 200 μl) were injected through injection valve using open valve mode. Table.4 tabulates the average response of three successive measurements, the arrival time of sample segment to the flow measuring cell (sec) and base width of response Δt_B (sec). The relative standard deviation and the confidence interval of the average response at 95% confidence level. It was noticed that any increase in the sample volume up to 140μl led to an increase in the height of responses as shown in figure-7-A. While figure-7-B shows a kind of response profile of variables sample volumes showing that above 140 μl sample volume there is an increase in the response base width Δt_B(min) (i.e. increase analysis time). This might be attributed to the long duration of reacting sample segment (i.e. colored species) in front of a detector, Δt the same time restriction of color segment to passes through out the flow measuring cell. Therefore, 140μl was found to be the most suitable sample volume for this work.

Table.4- Effect of the variation of sample volume on the transducer energy response for determination vanadium (V) 200 mg.L^{-1}, pyrogallol 1 mmol.L^{-1}, flow rate 1.8 mL.min^{-1}

t*	Base width Δt_B (sec)	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2,n-1} \sigma_{n-1}/\sqrt{n}$	RSD%	Transducer energy response expressed as average peak heights (n=3) $\bar{y}_i$ in (mV)	Sample volume μl
12	66	322±4.975	0.621	322	26
13.2	72	376±2.487	0.266	376	45
15	78	400.67±7.599	0.762	400.67	100
18	80	455±2.487	0.2197	455	140
18	99	465.67±5.177	0.456	465.67	200

t* = Departure time for sample segment from injection valve to the measuring cell
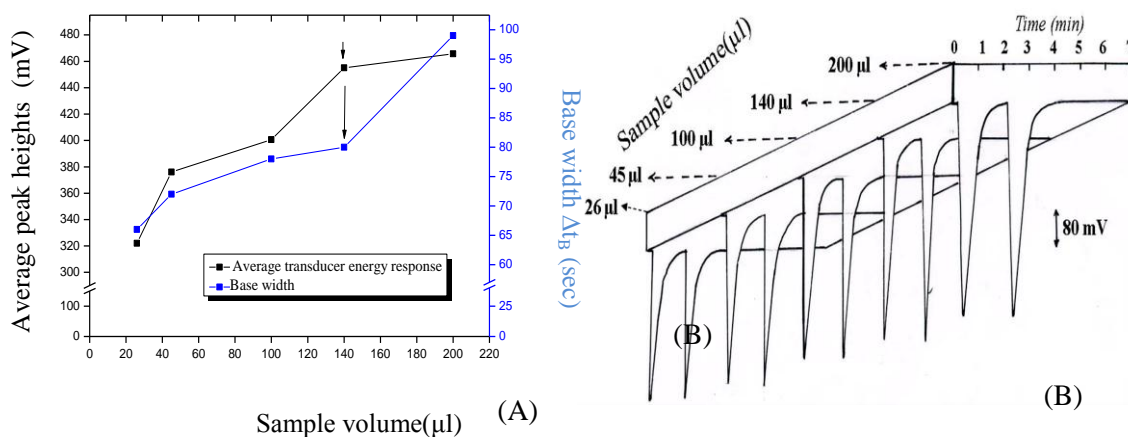
Figure 7- Effect of the variation of sample volume on the A- Transducer energy response expressed as peak heights in (mV) B- Response profile   average rate

Effect of Purge time

Using the optimum parameters achieved in pervious section. A study was carrier out to establish the optimum allowed permissible time for the sample segment to be injected from the injection valve 3,7,9,11 and 15 sec were used for this study in addition to allowed the injection valve in the open mode.Figure-8-A,B. shows the continuation of the increase the height of response with increase of injection time up to 9 sec, the reafter there was no significant differences in height response. A decrease in response when using less than 9 sec was might be attributed to the incomplete purge time of sample segment from sample loop in the injection valve**.** Above 9 sec, a decrease was attributed to the resistance of flow due to the passage through the injection valve. Therefore,9 seconds as a purge time was chosen as optimum to the completely purge of the sample from sample loop for the next studies. The obtained results were tabulated in table-5.

Table.5- Effect of the variation of purge time on the transducer energy response

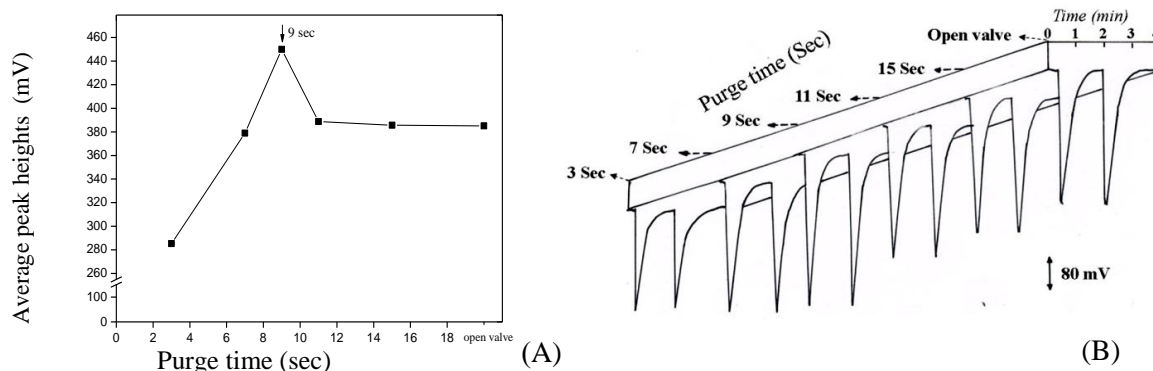| Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2,n-1}\, \sigma_{n-1}/\sqrt{n}$	RSD%	Transducer energy expressed as average peak heights (n=3) $\bar{y}_i$ in (mV)	Purge time Sec
285.33±3.799	0.535	285.33	3
6.581±397	0.698	379	7
4.975±450	0.444	450	9
388.67±5.744	0.594	388.67	11
385.67±5.178	0.539	385.67	15
385±2.487	0.259	385	Open valve

Figure8- Effect of the variation of purge time on A- Transducer energy response expressed as average peak heights in (mV) 1.8 mL.min^{-1},140 μl B- Response profil

Effect of reaction coil

The reaction coil length has a large role in the homogenization and completion of chemical reaction. The effect of reaction coil length on response profile was studied. Variable coil length $0 – 100$ cm was used as this range of length comprises a volume of $0 – 0.785$ mL which connected after Y- junction directly in flow system figure-1, optimum concentration of pyrogallol 1 mmol.L^{-1}, flow rate 1.8 mL.min^{-1} and 140 μl sample volume table-6 shows all the obtained results of coil length effect on energy transducer energy response, peak base width (Δt_b), and vanadium concentration after dilution, as shown in column 9. It can be seen that an decrease in peak height with increase coil length, increase of the Δt_b, and arrival time of injected sample from injection valve to the measuring flow cell, which might probably attributed to the increase effect of dilution and dispersion on colored segment and continuous longer time duration of colored species in front of detector. Figure-9-A,B shows the effect of coil length on transducer energy response and response profile. All these previous study indicated that no delay reaction coil is necessary for the completion of reaction

Table.6- variation of coil length on transducer energy response

Coil length (cm)	Volume (mL) $r^2\pi$ h, r =0.5 mm	transducer energy response expressed as Average peak heights n=3, $\bar{y}_i$ (mV)	RSD %	Confidence interval of the average response $\bar{y}_i \pm t_{0.05/2,\ n-1}\ \sigma_{n-1}/\sqrt{n}$	t^* (sec)	Δt_b (Sec)	V_{add} (mL)	[Vanadium(V)] mg.L^{-1} after dilution
0	0	451	0.222	451 ± 2.487	12	78	0.86	32.56
30	0.235	336	0.687	336 ±5.744	18	84	1.22	22.95
60	0.471	292	0.593	292 ± 4.308	21	87	1.4	20
100	0.785	262	0.769	262 ± 4.975	30	90	1.94	14.43

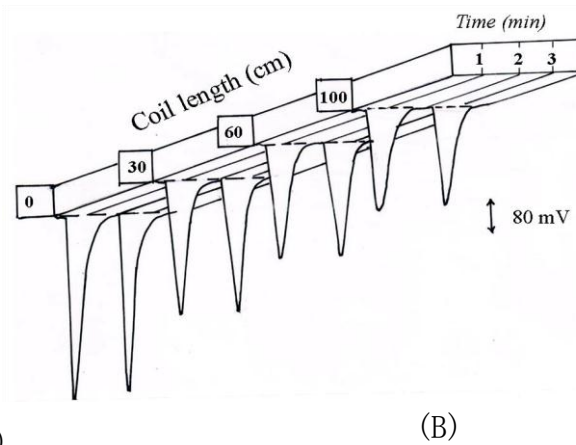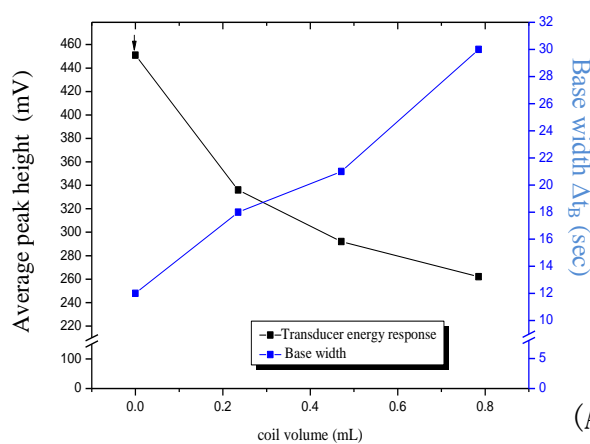$t^* =$ Departure time for sample segment from injection valve to the measuring cell

Figure9-Effect of the coil length on the A- Transducer energy response and base width B- Response profile
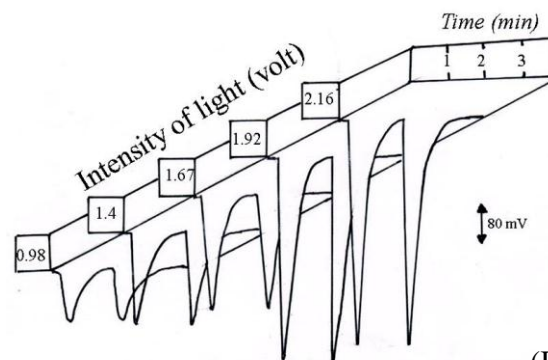
Intensity of light

Variable intensity of light source was used (0.98-2.16) volt by changing of light intensity channel in Ayah 6SX1-T-2D-solar cell CFI analyser operation where read by AVO-meter. The optimum condition were used 1 mmol.L^{-1} of pyrogallol concentration, 200 mg.L^{-1} of vanadium ion, flow rate 1.8 mL.min^{-1} and 140 μl sample volume. The obtained results tabulated in table-7 which shows that an increase in the peak height with increase light intensity. Therefore 2.16 volt was chosen as optimum voltage that can be supplied to give a better reproducible outcome as shown in figure-10-A,B.

Table 7: Effect of intensity of light on the transducer energy response

Intensity of light Volt	Transducer energy expressed as average peak heights (n=3) $\bar{y}_i$ in (mV)	RSD%	Confidence interval at (95%) $\bar{y}_i \pm t_{0.05/2,n-1} \, \sigma_{n-1}/\sqrt{n}$
0.98	115.53	0.360	115.53±1.035
1.4	200.93	0.501	200.93±2.504
1.67	255.87	0.705	255.87±4.486
1.92	450.67	0.462	450.67±5.177
2.16	500	0.400	500±4.975
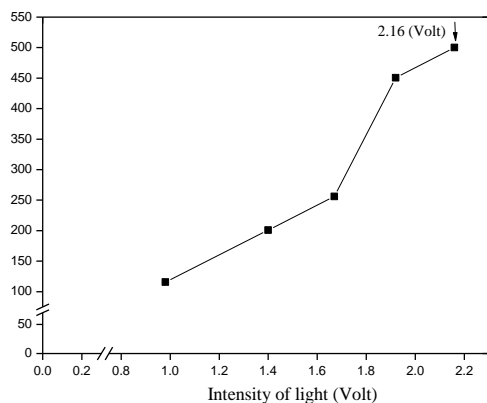
Figure 10-Effect of the varation of light intensity on the A- transducer energy response expressed as peak heights in (mV) B- Response profile

Calibration curve

Under the optimum condition achieved, a series of solutions for vanadium ion (1-500 mg.L^{-1}) were prepared and each measurement was repeated three times. Transducer energy response of the average peak heights (mV) was plotted against the concentration of vanadium ion. A straight-line graph from 1-200 mg.L^{-1} of vanadium ion was obtained as shown in figure-11. Above 200 mg.L^{-1} the value for correlation coefficient will decrease and deviate from linearity most probably due to the high intensity of the colored species in front of the detector in addition to the effect of inner filter of colored species; which might probably lead's to minimize the transmitted light. The results were tabulated in table-8
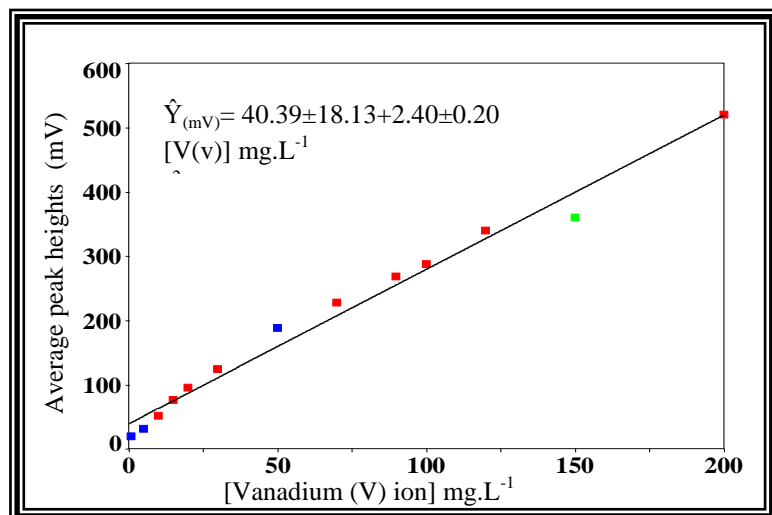

Figure.11- Calibration graph for the variation of vanadium (V) concentration on the transducer energy response by linear equation using Ayah 6SX1-T-2D Solar- CFI analyse

Table 8- Summary of linear regression[24,25] for the variation of energy transducer response with vanadium (V) concentration using first degree equation of the from $\hat{Y} = a+bx$ at optimum conditions.

Calculated t-value $\dfrac{/r/\sqrt{n-2}}{\sqrt{1-r_2}}$	t_{tab} at 95 % , n-2	R r^2%	$\hat{Y}_{(mV)}=a\pm s_a t+b\pm s_b t$[vanadium(V)] mg.L^{-1} At confidence interval 95%, n-2	Range of [vanadium(V)] mg.L^{-1} n=13	Measured vanadium(V) mg.L^{-1}
2.201<<26.066	0.9920	98.41	40.39±18.13+2.40±0.20[vanadium(V)] mg.L^{-1}	1-200	1-500

Limit of detection

Limit of detection for vanadium ion was calculated through three method: 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 tabulated all these calculation value of detection limit for 140 µL sample volume.

Table 9- limit of detection for vanadium(V) at optimum parameters depend on the different approach

Practically Based on the gradual dilution for the minimum concentration	TheoreticalBased on the value of slope x=3s$_B$/slope	Theoretical based on the linear equation $\hat{Y}=Y_B+3s_B$
70 ng/sample	1.75 ng/sample	3.49 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, $\hat{Y}$= estemited value

Repeatability

The repeatability of measurement and the efficiency of homemade Ayah 6SX1-T-2D solar analyser were studied at fixed concentration of vanadium ion, mainly one concentration was used 90 mg.L^{-1} ,at optimum parameters. The repeated measurements for five successive injections were measured and obtained results were tabulated in table-10 which shows that the percentage relative standard deviation was less than 1%, while figure-12 shows the response-time profile for the used concentrations.

Table 10- repeatability of energy transducer response for vanadium(V) at optimum parameters.

[vanadium ion] mg.L^{-1}	Average response $\bar{y}_i$(mV)	RSD %	$\bar{y} \pm t_{0.05/2,n-1}\ \sigma_{n-1}/\sqrt{n}$ At confidence interval 95%	NumberOf injection
90	267.2	0.811	268.8±2.692	5

$t_{0.05/2,n-1=}$ (2.776)
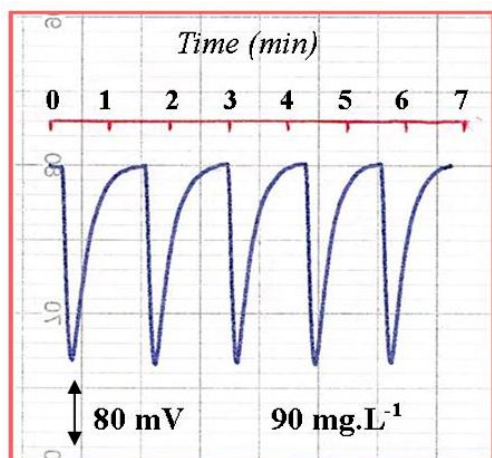
Figure 12- Response-time of five successive repeatable measurements of vanadium (V) concentration (90 mg.L^{-1}), 140 µL

Calibration graph of Classical method

   Calibration graph of classical method[26] was made to the determination of vandium(V) from 1-30 mg.L^{-1} after fixing the optimum parameters. Table.11 tablulates all the obtained data for the classical method, while table .12 shows the comparsion of both methods . The results indicated that the proposed method was more sensitive than the classical method.

Table 11-summary of calibration graph results for the determination of vanadium(V) ion by vanadium (V)-pyrogallol-H_3O^+ system at 427 nm and limit of detection[26]

Limit of detection mg . L^{-1}			Calculated t-value $\dfrac{/r/\sqrt{n-2}}{\sqrt{1-r_2}}$	t_{tab} at 95 % , n-2	r r^2%	Equation of calibration curve at 95%,n-2 $\hat{Y}=a\pm s_a t+b\pm s_b t[vanadium(V)]$	Linear dynamic range vanadium(V) mg.L^{-1}
x=3s$_B$/slope	$\hat{Y}$=Y$_B$+3s$_B$	Practically					
0.61	5.67	0.5	2.015<<13.97		0.9874 97.50 %	0.051±0.123+0.049±0.0068[vanadium (V)]	1-30

Table 12- Summary of result compared between Classical method and present method

Ayah 6SX1-T-2D solar analyzer FIA	Classical method	Analytical parameter
98.41	97.50	r^2%:linearity percentage
1-200 mg.L^{-1}	1-30 mg.L^{-1}	Linear dynamic range
2.40	0.049	Sensitivity (b)
40.39	0.051	Intercept (a)
70 ng/sample	0.5µg.mL^{-1}	Limit detection practically
40 µl1	5 mL	Sample volume
< 1%	1.2 %	Repeatability (n=5)RSD%

Determination of vanadium(V) ion in water samples

  Two methods were used to the determination vanadium(V) ion in a random river samples from Baghdad suberb. The first method was an Ayah 6SX1-T-2D Solar CFI analyser while the second method was used the classical spectrophotometric method via the measurement of λ_{max} (427 nm) . A series of solutions were prepared of each sample by transferring 5 mL to each of the five volumetric flask (25 ml), followed by the addition of 0,2.5,3.75,5,6.25 mL from 200 mg.L^{-1} standard solution of vanadium(V) ion in order to have the concentration range from (0-50) mg.L^{-1}. Flask no.1 is the sample volume. Table-13 shows the summary of standard additions method results from the three samples with the amount of vanadium (V) in water samples. Table-14 shows a paired t-test which compared the methods used for analysis from differently compares populated samples at 95% confidence interval. It can be noticed from the column no.9 in table.14 that the calculated t$_{value}$ is less than the critical t$_{value}$ (tabulated t-value at df=2 which equal at 4.303). Therefore, it can be regarded that there is no significant difference in using the two methods i.e: the newly developed instrument can be used as an alternative of the commercially available instrument.

Table 13- Results for the determination of vanadium (V) in real sample by two methods using standard addition

Calculated t-value $\dfrac{/r/\sqrt{n-2}}{\sqrt{1-r_2}}$	t_{tab} at 95 %, n-2	Vanadium mg.L^{-1} In 25 ml In 250 ml In 500ml	r r^2%	Equation of standard addition curve at 95%,n-2 $\hat{Y}_i = a \pm s_a t + b \pm s_b t[X]$	Type of Sample	Sample no
AYAH 6SX1-2D Solar CFIA						
(classical method Absorbance measurement)						
3.182<<10.029		5.49 27.45 13.73	0.9854 97.10 %	20.32±38.607 + 3.70±1.1748 [X]	of University Baghadad	1
3.182<<29.985		5.53 27.67 13.84	0.9978 99.56%	0.05±0.011 + 0.01±0.001 [X]		
3.182<<12.759		6.54 32.25 16.125	0.9909 98.19%	23.19±29.041+3.54±0.884 [X]	Alratuania	2
3.182<<10.414		6.47 32.35 16.18	0.9821 96.44%	0.032±0.0167 + 0.005±0.0015 [X]		
3.182<<10.723		6.02 30.1 15.05	0.9872 97.46%	20.59±33.37+ 3.42±1.015 [X]	Al-Dura	3
3.182<<12.475		5.91 29.55 14.78	0.9874 97.49%	0.04±0.020 + 0.01±0.0018 [X]		

$\hat{Y}_i$ = estimated value for energy transducer response (mV) or absorbance, [X]: [vanadium (V)] mg.L^{-1}, r= correlation coefficient, r^2 % = linearity percentage

Table.14- Paired t-test for Ayah 6SX1-T-2D solar analyser with classical method using standard addition method for determination of vanadium (V) in river samples

No of sample	Concentration of vanadium mg.L^{-1}				Xd	$\overline{X}d$	σ_{n-1}	$t_{cal} = \overline{X}d \sqrt{n} / \sigma_{n-1}$ at 95 %	t_{tab} at 95%
	500 mL	250 mL	After drow 5 mL and dilution to 25 mL						
			FIA	Classical method					
1	13.73	27.45	5.49	5.53	-0.04	0.047	0.078	1.044<<4.303	
2	16.13	32.25	6.54	6.47	0.07				
3	15.05	30.1	6.02	5.91	0.11				

Conclusion

In this research article, it was clear that a new method of analysis with a new mode of instrumentation that is capable for determination of vanadium (V) ion in water samples successfully at 30 samples through put per hour. The standard additions method was used to avoid matrix effects. Also, this method can be applied to nano determination of vanadium (V) ion with a high sensitivity without needing for heating or extracting.

References

1. Cintas, P. **2004**.The road t to chemical names and eponyms: discovery, priority, and credit. *Angew Chem Int Ed Engl*,43, pp: 5888-5894.

2. Cruywagen, J. J. Heyns, J. B and Westra, A. N. **1996**. Protonation Equilibria of Mononuclear Vanadate: Thermodynamic Evidence for the Expansion of the Coordination Number in VO(2)(+) *Inorg. Chem*,6, pp: 1556-1559.

3. Melwanki,M.B. Seetharamappa, J. and Masti, S. P. **2001**. Spectrophotometric determination of vanadium (V) in minerals, steels, soil and biological samples using phenothiazine derivatives. *Anal. Sci*,17, pp: 979-982.

4. Crans, D. C. Gottlieb, M. S., Tawara, J. Bunch, R. L. and Theisen, L. A. **1990**. A kinetic method for determination of free vanadium (IV) and vanadium (V) at trace level concentrations. *Anal. Biochem*,188, pp: 53-64.

5. Abbaspour, A. and Mirzajani, R. **2005**. Application of spectral *β*-correction method and partial least squares for simultaneous determination of V (IV) and V (V) in surfactant media. *Spectrochimica Acta Part A*, 64, pp: 646–652.

6. Taylor, M. J. C. & Vanstaden, J. F. **1995**. Determination of vanadium (IV) and vanadium (V) by formation of a transient mixed-valance complex in a flow injection manfold. *Anal. Chim. Acta*, *307*, pp: 1-13.

7. Safavi, A. Abdollahi, H. Sedaghatpour, F. and Zeinali, S. **2000**. Kinetic Spectrophotometric determination of V (IV) in the presence of V (V) by the H-point standard addition method. *Anal. Chim. Acta*. 409, pp: 275-282.

8. Lander, J. Steiner, D.W. Anderson, D.H. and Dehm, R.L. **1971**. Spectrographic Determination of Elements in Airborne Dirt. *Appl. Spectrosc*, 25, pp: 270-275.

9. Eissa, E.A. Rofail, N.B. Ali, R.A. and Hassan,A.M. **1996**. Investigation of an egyptian phosphate ore sample by neutron activation analysis technique. *Radiat. Phys. Chem*, 47, pp: 705-708.

10. Kucera, J. J. Lener, L. S. and Horakova, J. **1996**. Air pollution and biological monitoring of environmental exposure to vanadium using short- time neutron activation analysis.*J. Trace Microprobe- Tech*, 14, pp: 191-201.

11. Wuilloud, R. G. Salonia, J.A. Ga´squez, J.A. Olsina, R. A and Martinez ,L.D .**2000**. On-line pre-concentration system for vanadium determination in drinking water using flow injection-inductively coupled plasma atomic emission spectrometry. *Anal Chim Acta*, 420, pp: 73-79.

12. Wuilloud, R. G. Salonia, J. A. Olsina, R. A and Martinez, L. D. **2000**. Determination of vanadium(V) in drinking water by flow injection and pre-concentration in a knotted reactor by inductively coupled plasma optical emission spectrometry with ultrasonic nebulization. *Spectrochim Acta B,* 55, pp: 671-680

13. Wann, C. C and Jiang, S. J. **1997**. Determination of vanadium species in water samples by liquid chromatography-inductively coupled plasma mass spectrometry. *Anal Chim Acta*, 357, pp: 211-218

14. Massoumi, A. and Tavallali, H.**1998**. Kinetic spectrophotometric determination of vanadium by catalytic effect on the indigo carmine-bromate reaction. *Anal. Lett*,*31*,pp: 193-206.

15. Ensafi, A. A. Amini, M. K. and Mazloum, M. **1999**. Spectrophotometric reaction rate method for the determination of trace amounts of vanadium (V) by its catalytic effect on the oxidation of Nile Blue with bromate. *Anal. Lett, 32*, pp: 1927-1937.

16. Gavazov, K., Lekova, V., Patronov, G. and Turkyilmaz, M. **2006**. Extractive-spectrophotometric determination of vanadium (IV/V) in catalysts using 4-(pyridylazo)-resorcinol and tetrazolium violet. *Chem. Anal. (Warsaw),51*, pp: 221-227.

17. Pyrzy nska, K and Wierzbicki, T .**2005**. Pre-concentration and separation of vanadium on Amberlite IRA-904 resin functionalized with porphyrin ligands. *Anal Chim Acta*, 540, pp: 91-94.

18. Ekinci, C and K€okl€u, €.**2000**. Determination of vanadium, manganese, silver and lead by graphite furnace atomic absorption spectrometry after preconcentration on silica-gel modified with 3-aminopropyltriethoxysilane. *Spectrochim Acta B*, 55, pp: 1491-1495.

19. Sanchez, R. G, Bettmer, J and Ebdon, L .**2004**. Development of a new method for the separation of vanadium species and chloride interference removal using modified silica capillaries- DIN-ICP-MS. *Microchem J* ,76, pp: 161-171.

20. Chen, Z. Owens, G. and Naidu, R. **2007.**Confirmation of vanadium complex formation using electrospray mass spectrometry and determination of vanadium speciation by sample stacking capillary electrophoresis. *Anal. Chim. Acta, 585,* pp: 32-37.

21. Vachirapatama, N. Dicinoski, G. W. Townsend, A.T and Haddad, P.R. **2002**. Determination of vanadium as 4-(2-pyridylazo)resorcinolhydrogen peroxide ternary complexes by ion-interaction reversedphase liquid chromatography. *J. Chromatogr. A,956*, pp: 221-227.

22. -Liu, E. Liu, Y and Cheng, J.**2002**. Ultrasensitive chemiluminescence detection of vanadium(IV) by capillary elecrophoresis. *Anal. Chim. Acta*, *456*, pp: 177-181**.**

23. Chen,G.N. and Huang,C.S.**1988**. A study of chemiluminescence of some acidic triphenylmethane dyes.*Talanta*,38 (8), pp: 625-631**.**

24. Miler,J.C.and Miller,J.N. **1988**. *Statistics for Analytical Chemistry*, 2ⁿᵈ, Ed., John Wiley and N.y. Sons.

25. Bluman,A.G.**1997**,*Elementary Statistics,*3ʳᵈ, Ed., WCB/MC Graw-Hill, New York

26. Nagam,S.T. **2008**. Spectrophotometric continuous flow injection analysis for determination of vanadium (V) ion in water samples by oxidation of pyrogallol expressed as Quadratic equation. *J. Nah. Uni*. 11(3).pp: 9-2