Chemiluminometric- CFIA for the Determination of Cobalt (ll) Ion in Commercial Cobalt-Molybdenum Catalyst (K F124-3E) Used in Desulphurization Processes of Petroleum Products via Multi Gel Beads Reactor.

Issam M.A. Shakir[1*], Zaineb F. Hassan.

Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

Abstract

Co(II) ion was determined by a new, accurate, sensitive and rapid method via a continuous flow injection analysis (CFIA) with a chemiluminescence reaction based on the oxidation of Luminol which is loaded on poly acrylic acid gel beads by hydrogen peroxide in presence of Cobalt (II) ion as a chemiluminescence catalyst. Chemical and physical parameters were investigated to obtain the best conditions. Linear dynamic range of Cobalt (II) ion was from $0.1\text{-}20.0$ $\mu g.ml^{-1}$ with a correlation coefficient $r = 0.9758$, limit of detection (L.O.D) 0.2 ng/sample from the step wise dilution of lowest concentration in the calibration graph with the percentage relative standard deviation for 3 $\mu g.ml^{-1}$ Co(ll) solution is 0.8537% (n=5). The method was applied successfully for the determination of Co (II) ion in CoMo catalyst type (K F124- 3E).

Keywords: Chemiluminescence, Flow injection analysis, gel beads, Cobalt (ll) Ion., CoMo Catalyst (K F124- 3E).

التحليل بالحقن الجرياني المستمر لتفاعل كيموتألقي بمفاعل متعدد حبيبات الهلاميه لتقدير ايون الكوبلت الثنائي في العامل المحفز التجاري (3E- K F124) CoMo ألمستخدم في عمليات أزالة الكبريت في المنتجات البترولية.

عصام محمد علي شاكر*, زينب فلاح حسن

قسم الكيمياء, كلية العلوم , جامعة بغداد , بغداد , العراق

الخلاصة

تم تقدير ايون الكوبلت بطريقة جديدة ، دقيقه ، حساسه و سريعة بواسطة الحقن الجرياني المستمر مع تفاعل البريق الكيمياوي الناتج من اكسدة اللومينال المحمل على حبيبات متعدد حامض الاكريلك بواسطة بيروكسيد الهيدروجين و بوجود ايون الكوبلت الثنائي كعامل محفز لتفاعل البريق الكيمياوي . تم دراسة كافة المتغيرات الفيزيائية و الكيميائية . العلاقة الخطية لمنحني المعايرة لايون الكوبلت الثنائي تمتد بين 0.1 – 20.0 مكغم. مل$^{-1}$ و بمعامل ارتباط 0.9758 . حدود الكشف كانت 0.2 نغم/ نموذج من التخفيف التدريجي لاقل تركيز في منحنى

_____

*Email: issam.shakir@yahoo.com

المعايرة مع انحراف قياسي نسبي مئوي   0.8537% لتركيز 3 مكغم. مل[1-] من محلول الكوبلت الثنائي . طبقت

الطريقة بنجاح لتقدير ايون الكوبلت الثنائي في العامل المساعد (3E -K F124) CoMo.

Introduction

Cobalt is classified as a strategic and critical metal because of its applications in defense-related industries. It's used to make heat resistant super alloys, corrosion and wear resistant alloys, and magnets. Cobalt compounds are important as drying agents for paints, varnishes and inks. These compounds have been used for centuries to impart a rich blue color to glass and ceramic[1,2] .Supported Co-Mo sulfides catalysts have been used in petrochemical processes, generally in hydro desulphurization reactions (HDS).these (CoMO$_X$) catalysts are typically 3-5% Co oxide (Co$_3$O$_4$) and 14% MoO$_3$, the balance being Al$_2$O$_3$ Alumina. HDS processes common to all refineries, in it the feedstock (crude oil fraction) and hydrogen are passed over a catalyst at elevated temperature and pressure. The aim is to convert the organic sulfur to hydrogen sulfide (H$_2$S) [3-5].Cobalt comprises about 0.02 percent of earth's crust and it's produced as a by-product of either nickel or copper [6].

There are varieties of methods concerning the determination of trace levels of Cobalt, Demonstrating the importance of this element. The most common methods based on atomic absorption spectrometry, these methods usually performed after a separation and pre-concentration steps, also these methods involve the risk of sample contamination and analyte loss [7-11].Voltametric techniques proving to be useful even at low levels of Cobalt, however they suffer from interferences of various electro active compounds which are co-oxidized at the applied potential [12,13].

Among the techniques that are suitable for the determination of Co (II) ion is the inductively coupled plasma [14] and other methods based on UV-vis spectrophotometry [15-18].

Chemiluminesence (CL) is defined as electromagnetic radiation produced when a chemical reaction yields on electrochemically excited intermediate or product, which either luminescence (direct CL) or donates its energy to another molecule responsible for the emission (indirect CL)[19,20]. The advantages of CL methods combined with flow injection analysis include super sensitivity, rapidity, wide dynamic range, simple instrumentation and easy automation [21-23]. CL methods have been employed for the determination of Co (II) ion; these methods are based on the catalytic effect of Co (II) ion in the reaction between Hydrogen peroxide and luminol as a luminescence agent [24-28].

Experimental

Chemicals:

All chemicals were used of analytical-reagent grade while distilled water was used to prepare the solutions. A standard solution of 1000 µg.ml^{-1} Cobalt (II) ion as Co (NO$_3$)$_2$.6H$_2$O (291.03 g.mol^{-1}, BDH) was prepared by dissolving 2.4691g in 500 ml distilled water. A stock solution (1×10^{-3} mol.L^{-1}) of Luminol solution (5-amino phthalylhydrazide) C$_8$H$_7$N$_3$O$_2$ (177.16 g.mol^{-1},BDH) was prepared by dissolving 0.0885g in 500 ml of 0.05mol.L^{-1} solution of sodium carbonate Na$_2$CO$_3$(105.97 g.mol^{-1} , BDH), prepared by dissolving 2.6493g in 500 ml distilled water. A stock solution of hydrogen peroxide H$_2$O$_2$ (1×10^{-2}mol.L^{-1}) was prepared by pipetting 3.7 ml of hydrogen peroxide (20% vol., 34.01 g.mol^{-1}, Romil LTD.) and complete the volume with distilled water to 500 ml volumetric flask. Hydrogen peroxide molarity was fixed in sulfuric acid medium (1:1) with potassium permanganate solution KMnO$_4$ (0.1 mol.L^{-1}) (158.03g.mol^{-1}, Hopkin&William) was prepared by dissolving 7.9015g in 500 ml of distilled water. This solution was standardized previously against Sodium oxalate solution Na$_2$C$_2$O$_4$ 0.1 mol.L^{-1} (134.0g.mol^{-1}, BDH) prepared by dissolving 3.35g in 250 ml distilled water. Gel beads that are having weight range between 35.0-39.0.mgm, were washed and swelled in distilled water then dried using homemade drying cabinet. The dehydration process need about 132 hours at 45^{0}C and relative humidity 8%. The sorted gel beads kept in clean and dry containers based on their weight; which corresponds with diameter. All these treatments of gel beads were made in order to obtain and in turn use regular unbiased sample of beads.

Sample preparation

A 100 ml solution of CoMo (K F124-3E) catalyst was prepared by dissolving 1.0 g of the Catalyst containing 0.04 % wt. of CoO in 25 ml of concentrated nitric acid (70 %, 1.42g.mol^{-1}, BDH). This

solution was heated on IR heater until the volume of acid reached to its half volume, then a 50 ml of distilled water was added. Heating was continued until just about dryness. The rest of the remaining dissolution product was filtered through Whitman 595 filter paper to 100 ml volumetric flask. 2.02 ml of this dissolving product was transferred to 100 ml volumetric flask and a series of solutions were prepared for standard addition curve.

Apparatus

The flow system consist of variable speeds peristaltic pump- 4 channels (Switzerland) an Ismatic type ISM796. A rotary 6-port injection valve (Teflon) (Rheodyne, U.S.A.) with sample loop of 1mm i.d. Teflon, variable length. Electronic measuring system consist of photomultiplier tube PMT (Hama Matsu R372, Japan) enclosed with the chemiluminescence cell by a black leather in order to reduce the background interferences. DC voltage power supply (0-1.6 KV) type (JOBIN YVON- France). Dual detector (United Detector Technology, U.S.A.) capable of measuring pA –nA level. The read out of the system composed of x-t potentiometric recorder (1-500 mV) (KOMPENSO GRAPH C-1032) SIEMENS (Germany). The gel bead cell unit (GBCU).

Methodology

Figure 1 shows the illustrative flow gram of the manifold system that was used for the determination of Cobalt (II) ion.
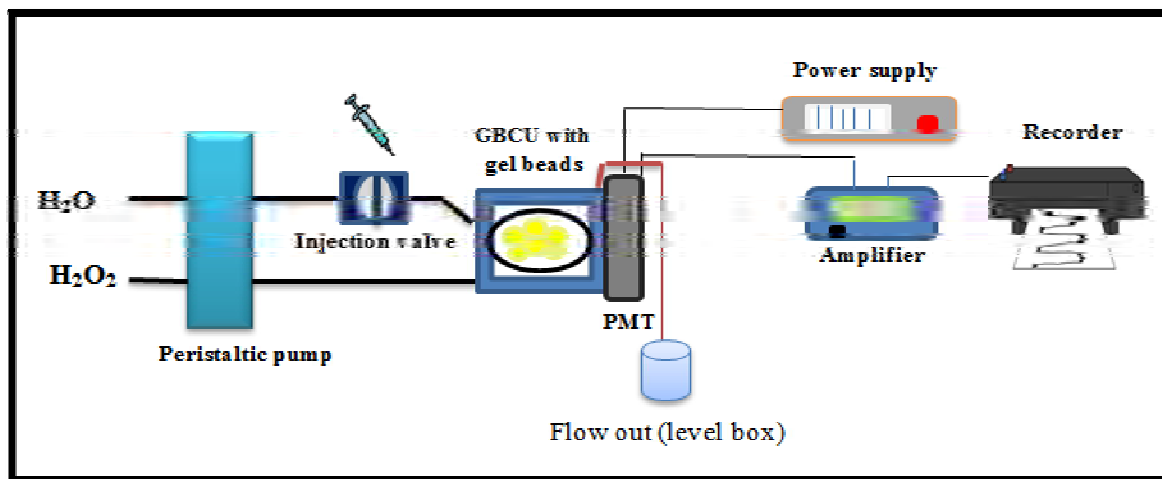
Figure 1- Schematic diagram of Continuous Flow Injection Analysis system with gel beads cell unit (GBCU) for determination of Cobalt (II) ion.

It is simply composed of two lines, the first line supplies the carrier stream which is distilled water at flow rate of 2ml.min^{-1} which leads to the injection valve to carry the segment of Co(II) ; while the second line supplies hydrogen peroxide at flow rate of 2.65 ml.min^{-1} . These two lines met and mixed at the GBCU which will supply the donor molecule i.e. Luminol that is necessary for the completion of the CL-reaction, Luminol will be released by the action diffusion from within the gel beads to the surrounding environment in which Cobalt (II) ion and Hydrogen peroxide will mix and the process of Chemiluminescence will take place. Two inlets were used (care was take due to the expansion of the gel beads). Gel beads were previously soaked in Luminol solution (1×10^{-3}mol.L^{-1}) dissolved in 0.05 mol.L^{-1} of sodium carbonate. 60 μL as sample volume of Co (II) ion was injected for each measurement. The duration of injection period was 50 seconds for complete sample discharge. Three minutes as a time lag period was left between each two successive measurements. The obtained CL-response was assayed via photomultiplier tube (PMT) output in triplicate form, while the converted potential difference was recorded on x-t potentiometric recorder. The mechanism of Luminal oxidation   by hydrogen peroxide in presence of Co (ll) ion as catalyst is shown in scheme 1 [29].
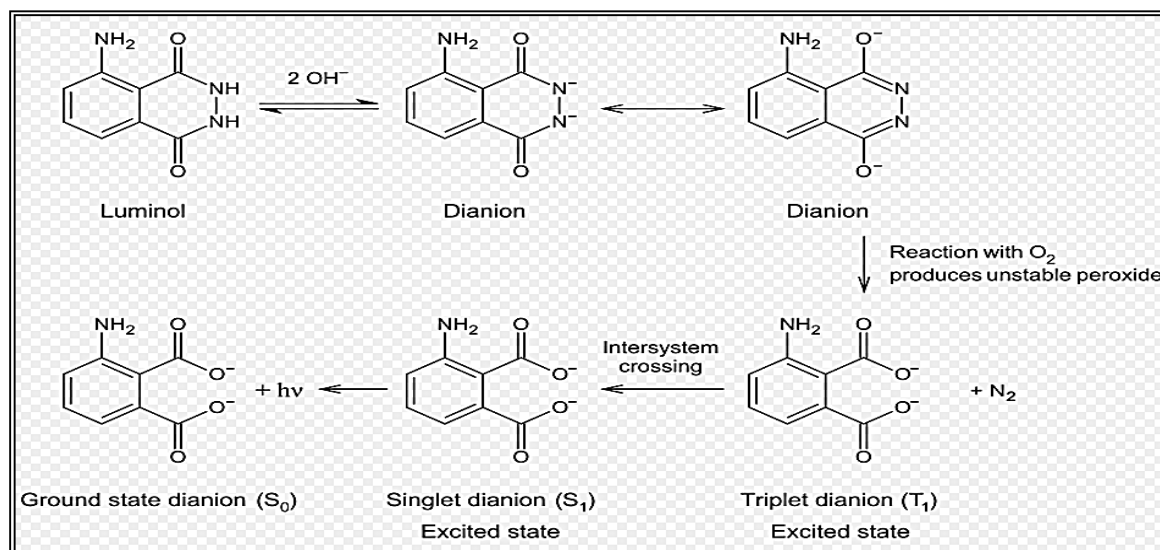
Scheme 1- proposed mechanism of Luminol$_{GB}$ –H$_2$O$_2$- Co (II) ion CL- system.

Results and discussion
Optimization of variables
   Chemical as well as physical parameters were studied by employing the flow injection manifold that was shown in fig.1, in order to obtain the optimum parameters for the conditions of the chemiluminescence reaction.
Chemical variables:
   Preliminary sets of experiments were curried out to decide the optimum possible, and workable range of Luminol solution concentration that will be fed to the gel beads to give a constant supply of donor is necessary for the completion of the CL-reaction. No CL-emission could be seen from the gel bead that is soaked in Luminol solution with the concentration less than 1×10^{-3}mol.L^{-1}, while no more concentrations of Luminol solution were used in order to avoid the deformation in poly acrylic acid beads structure.
   Therefore, this concentration was used to feed the gel beads inside the GBCU.
Hydrogen peroxide was used as an oxidant for Luminol to generate the CL-emission at the presence of Co (II) ion as a catalyst. Using a variable concentration of hydrogen peroxide 1×10^{-5}-5×10^{-4} mol.L^{-1} using open valve mode with a sample volume of 60μL at a flow rate of carrier and reagent stream 2ml.min^{-1} and 2.65 ml.min^{-1} respectively. A study was carried out to optimize the concentration of hydrogen peroxide that will be in use for the rest of this work. table.1 tabulates the obtained results and figure.2 A and B shows that 5×10^{-5}mol.L^{-1}of H$_2$O$_2$ was the optimum concentration.

Table1-Effect of [H$_2$O$_2$] on the CL-response expressed as average peak height (mV)

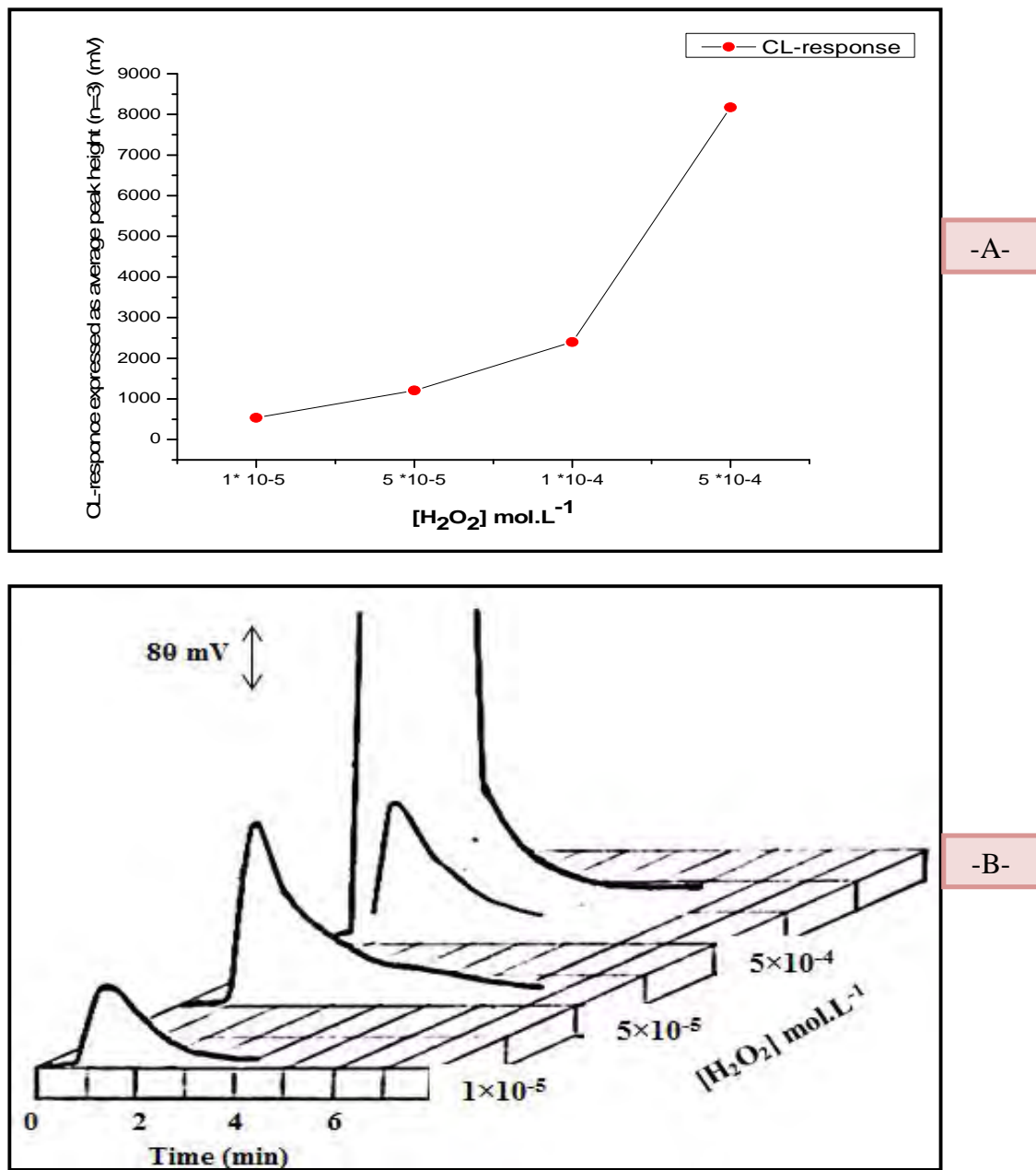| [H$_2$O$_2$] Mol.L^{-1}	CL-response expressed as peak height (n=3), (mV)	Average $\bar{y}_i$ (mV)	RSD%	Confidence interval of the mean at 95% $\bar{y}_i \pm t_{0.05/2,\,n-1}\, \sigma_{n-1}/\sqrt{n}$
1×10^{-5}	540, 540, 534	538	0.644	538 ± 8.602
5×10^{-5}	1220, 1200, 1210	1210	0.826	1210 ± 24.846
1×10^{-4}	2400, 2402, 2398	2400	0.0833	2400 ± 4.969
5×10^{-4}	8180, 8180, 8160	8173.333	0.141	8173.333 ± 28.688

Figure 2- Effect of $[H_2O_2]$ on: A- CL- response expressed as average peak height (mV),
-B- CL-response time profile.

Physical variables
Effect of applied photocathode voltage

Using the optimum concentration of H_2O_2 , 5×10^{-5} mol.L^{-1} with 60 µL of 5 µg.ml^{-1} of Co(II) as an injected sample segment, flow rate of carrier and reagent stream 2ml.min^{-1} and 2.65 ml.min^{-1} respectively , variable photocathode voltage expressed in applied DC voltage ranged from (400-700 V DC) was applied. The obtained results were tabulated in table 2. It was observed that an increase in the applied voltage leads to increase the intensity of the CL-emission. Therefore; 600 V DC was adopted as the optimum voltage that can be supplied to give a reasonable CL-response as shown in figure. 3. No more voltages were used since excess voltages may cause an increase in the electronic noise, thus leads to a decrease in response and increase in thermal noise.

Table 2- Effect of variation of the applied DC voltage to the PMT photocathode on CL-response expressed as current (nA)

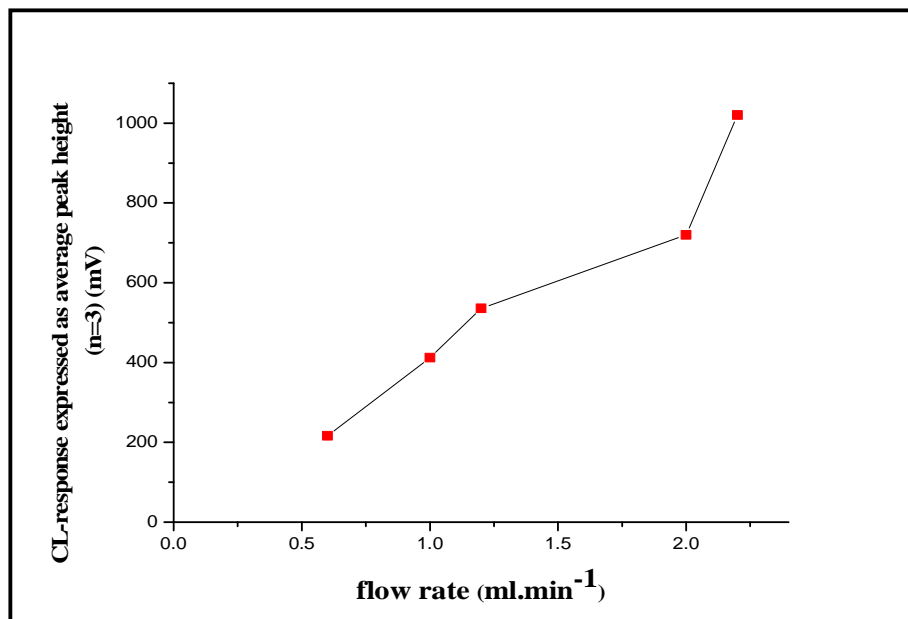| Applied voltage (V)[*]	CL-response expressed as current (n=4), (nA)	Average $\bar{y}_i$ (nA)	RSD%	Confidence interval of the mean at 95% $\bar{y}_i \pm t_{0.05/2,\,n-1}\,\sigma_{n-1}/\sqrt{n}$
400	2.97, 2.96, 2.98, 2.97	2.970	0.27	2.970 ± 0.0127
500	19.20, 19.00, 19.00, 18.90	19.025	0.66	19.025 ± 0.200
600	75.00, 75.200, 76.00, 74.90	75.275	0.66	75.275 ± 0.794
700	123.00, 122.60, 122.90, 122.80	122.825	0.14	122.825 ± 0.221

*VDC
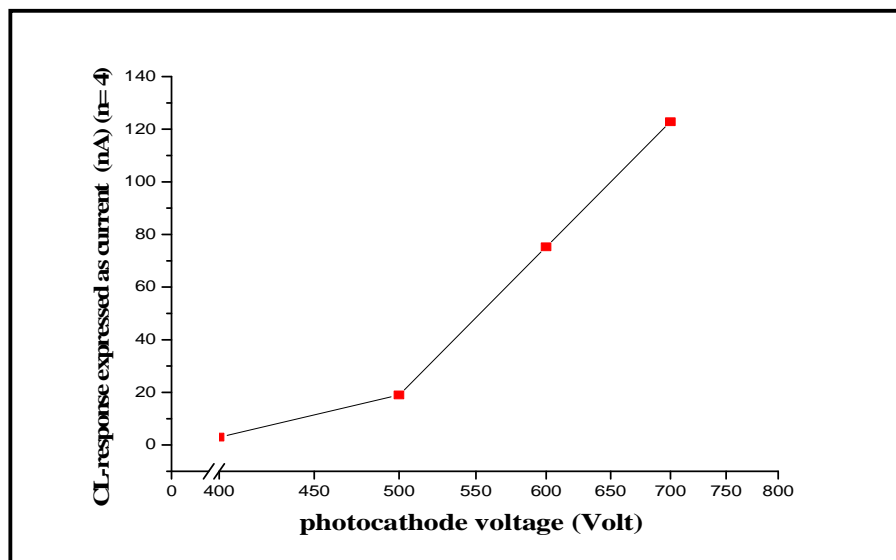
Figure 3- variation of CL- response versus photocathode voltage (Volt)
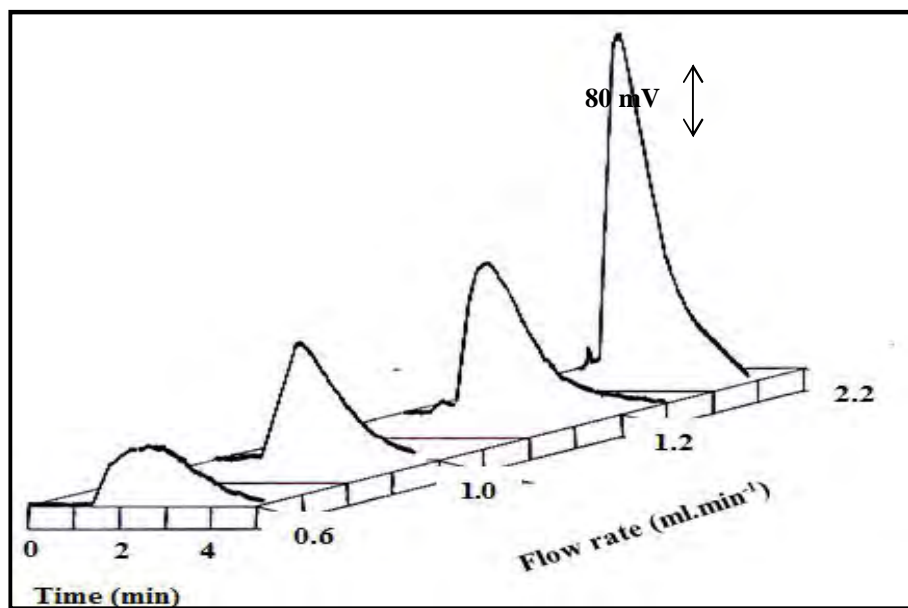
Effect of flow rate

Using the optimum parameters that were achieved in previous sections, 5 µg.ml^{-1}Co(II) ion and 60 µL as sample volume with variable flow rates ranged from 0.4- 3.5 ml.min^{-1} for carrier and reagent stream line were studied at 600 V DC photocathode voltage . Table .3 sums up the obtained results. Figure 4 (A,B) shows that the CL-response intensity increases with increasing flow rate, but due to the special design of the manifold and the saturation of the electronic system, a compromise was made between obtaining high CL-response with the consumption of reagents and ease of work . Therefore; a flow rate of 2 ml.min^{-1}, 2.65 ml.min^{-1} were chosen as optimum flow rate for the carrier and hydrogen peroxide stream line respectively.

Table 3- Effect of flow rate variation on CL-response (mV)

Pump speed indication approximate	Flow rate (ml.min^{-1})		Average CL-response expressed as peak height (n=3), $\bar{y}_i$ (mV)	RSD%	Confidence interval of the mean at 95% $\bar{y}_i \pm t_{0.05/2,\,n-1}\,\sigma_{n-1}/\sqrt{n}$
	Carrier Stream line	H_2O_2 stream line			
10	0.6	0.9	216	0.0	216 ± 0.0
15	1.0	1.4	412	0.971	412 ± 9.9356
20	1.2	1.8	536	0.0	536 ± 0.0
30	2.0	2.65	720	0.0	720 ± 0.0
35	2.2	3.1	1020	0.392	1020 ± 9.9356

Figure 4- Effect of variation of the flow rate on   A- CL-response expressed as average peak height (mV)
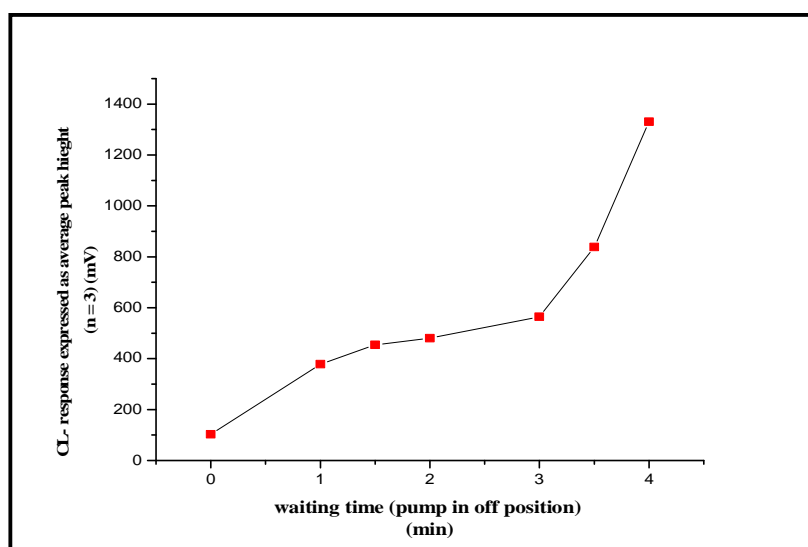 B- CL-response - time profile

Effect of recharging time

   A study was conducted to fix the optimum recharging time at stop-go mode of operation. The allowed recharging time for the liberation of Luminol to supply the reaction medium with the CL- donor from within the gel beads (diffused Luminol solution). Using the optimum parameters that were achieved in previous sections, a time laps of recharging period ranged from 0-4 minutes was used.
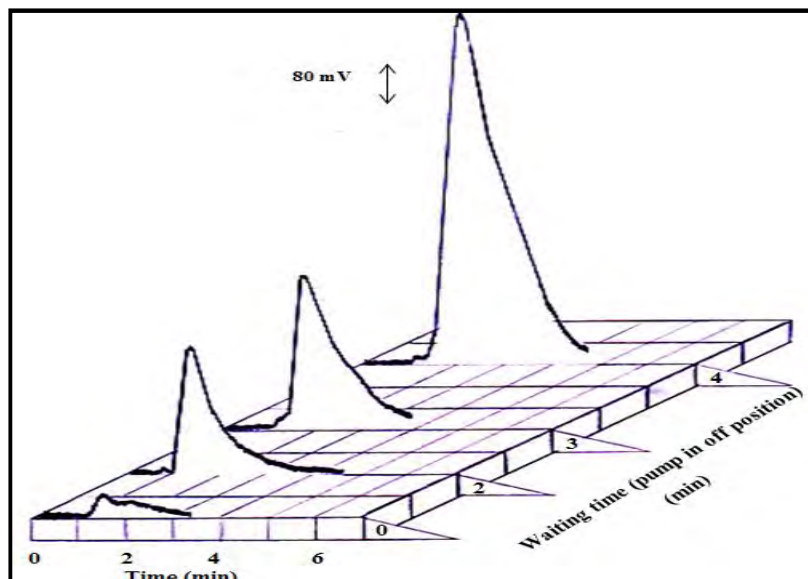
   Table. 4 summarize the obtained results. Figure 5 (A,B) shows that in general an increase in recharging time (waiting period till the next injection) gives higher CL-response which restricts the upper limit of sensitivity, suitability, and ease of working. Therefore, a waiting period of 3 minutes was adopted as an optimum recharging time.

Table 4- Effect of recharging time on CL-response.

Off pumping time(min.)	Average CL. responses expressed as peak height, $\bar{y}_i$, (n=3) (mV)	RSD%	Confidence interval of the mean at 95% $\bar{y}_i \pm t_{0.05/2, n-1} \, \sigma_{n-1}/\sqrt{n}$
0	102.667	2.249	102.667 ± 5.736
1	378.000	0.529	378.000 ± 4.970
1.5	454.333	0.458	454.333 ± 5.172
2	480.000	0.000	480.000 ± 0.000
3	564.667	0.737	564.667 ± 10.344
3.5	838.667	0.275	838.667 ± 5.736
4	1331.00	0.327	1331.00 ± 10.830

-A-

-B-

Figure 5- Effect of recharging time on: -A- CL-response expressed as average peak height (mV) -B- CL-response- time profile.
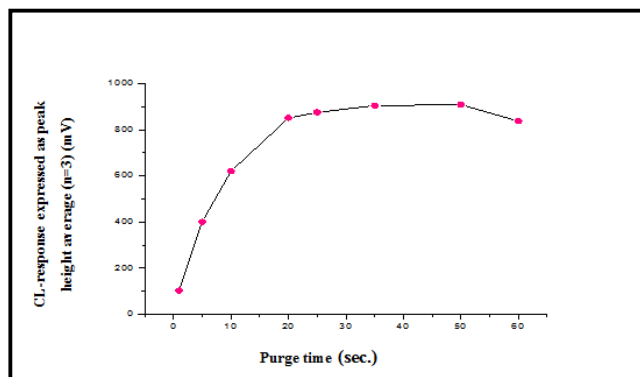
Effect of purge time

Variable purge times for the sample segment of 1-60 seconds were used for this study in addition to open valve mode. Using the optimum parameters, 600 V DC photocathode voltage, 2 ml.min^{-1} flow rate and 3 minutes as a recharging time. Sample volume of 60 μL was used with 5 μg.ml^{-1} of Co (II) ion.

Table 5 summarize the obtained results. Figure 6 shows that an increase in CL-response occurs due to the increased batch of sample volume injected from the sample loop through the carrier stream. Therefore; 50 seconds purge time was chosen as an optimum time to achieve a complete discharge of the sample from its loop.

Table5- Effect of variation of purge time on CL-response.

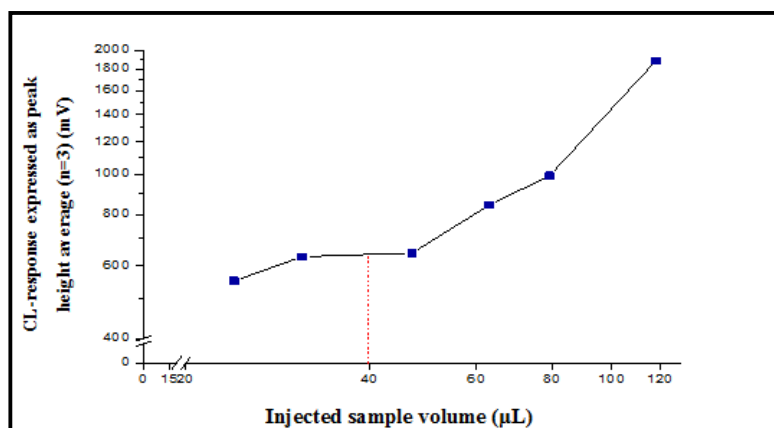| purge time (sec.)	CL-. response expressed as average peak height, $\bar{y}_i$, (n=3) (mV)	RSD%	Confidence interval of the mean at 95% $\bar{y}_i \pm t_{0.05/2,\ n-1}\ \sigma_{n-1}/\sqrt{n}$
1	103	2.569	103 ± 6.575
5	401	0.432	401 ± 1.071
10	620	3.226	620 ± 49.687
20	851.667	1.222	851.667 ± 25.857
25	875.667	0.287	975.667 ± 6.252
35	904.667	0.400	904.667 ± 10.344
50	908.333	0.168	908.333 ± 3.795
60	837	0.316	837 ± 6.575
Open valve mode	836.333	0.483	836.333 ± 10.039

-A-
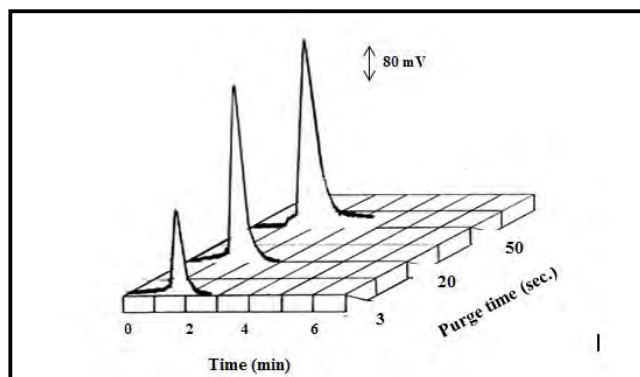
-B-

Figure 6- Effect of purge time on the: A- CL-response expressed as average peak height (mV).
B- CL-response -time profile.
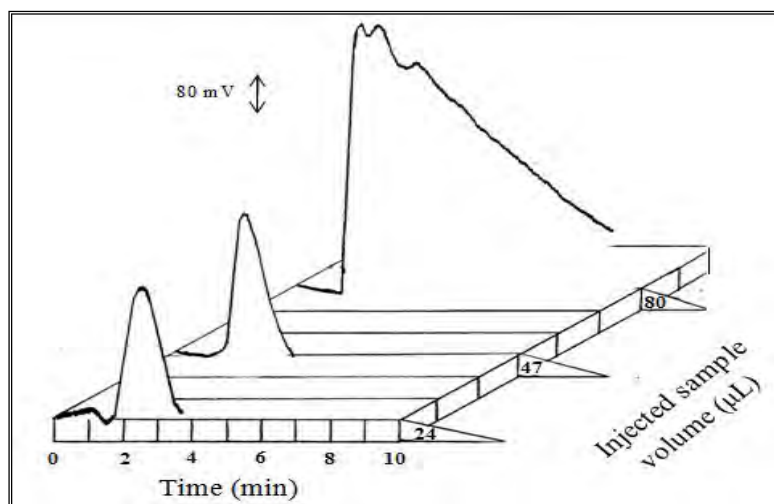
Effect of sample volume

   In order to establish the optimum sample volume, a study was conducted by using variable sample volumes 24-118 µL by changing the length of sample loop in the injection valve. Table.6 sums up the obtained results. Figure 7 A and B shows the plot of CL-response intensity versus change in sample volume µL. There is a gradual increase from 23µL up to 118 µL .Therefore; a sample loop of 5 cm which is equivalent to 40 µL was fixed as the optimum sample volume in order to obtain a regular CL-response.

Table 6- Effect of sample volume variation on CL-response.

Loop length (cm)	Injected sample volume (µL)	CL-. response expressed as average peak height, $\bar{y}_i$, (n=3) (mV)	RSD%	Confidence interval of the mean at 95% $\bar{y}_i \pm t_{0.05/2,\ n-1}\ \sigma_{n-1}/\sqrt{n}$
3	24	552	0.0	552 ± 0.0
4	31	632	0.316	632 ± 4.970
6	47	644.67	0.646	644.67 ± 10.344
8	63	845	0.473	845 ± 9.936
10	79	994.33	0.381	994.33 ± 9.406
15	118	1887	0.717	1887 ± 33.606

-A-

-B-

Figure7- Effect of variation of sample volume on:
A- CL-response expressed as average peak height (mV)
.B- CL-response -time profile.

Calibration graph and statistical parameters

At the established optimum conditions, a series of Co (II) ion solutions 0.1-20.0 $\mu g.ml^{-1}$ was prepared. Each measurement was repeated for three times. CL-response of average peak height (mV) was plotted against Co(II) ion concentration , a straight graph from 0.1-20.0 $\mu g.ml^{-1}$ of Cobalt ion (II) was obtained. All results were tabulated in table.7, while figure 8 shows an increase in CL-response intensity with the concentration of Co (II) ion, which might be attributed to the increase in number of the emitted species.

Table7 -Summary of calibration graph results for the determination of Co(II) ion by Luminol$_{G.B.}$- H_2O_2- Co(II) ion

Measured Conc. Of Co (II)ion ($\mu g.ml^{-1}$)	Linear dynamic range ($\mu g.ml^{-1}$) (n=16)	Linear equation $\hat{Y}i$ (mV) = a ± ts$_a$ +b ± ts$_b$ [Co(II)] $\mu g.ml^{-1}$ at confidence level 95% , n – 2	r , r^2%	t$_{(0.05/2),14}$ at 95% confidence limit	t$_{cal}$ t= $\frac{\|r\| \sqrt{n-2}}{\sqrt{1-r^2}}$
0.1 – 20.0	0.1 – 20.0	-24.869± 168.639 + 152.974 ± 19.639 [X]	0.9758, 95.2242%	2.1600 << 16.7192	

$\hat{Y}i$ (mV) =Estimated CL-response for (n=3), [x] = [Co (II)] $\mu g.ml^{-1}$, r = correlation coefficient, r^2% = linearity percentage., t$_{tab=}$t$_{0.05/2 , n-2}$ at 95% confidence level.
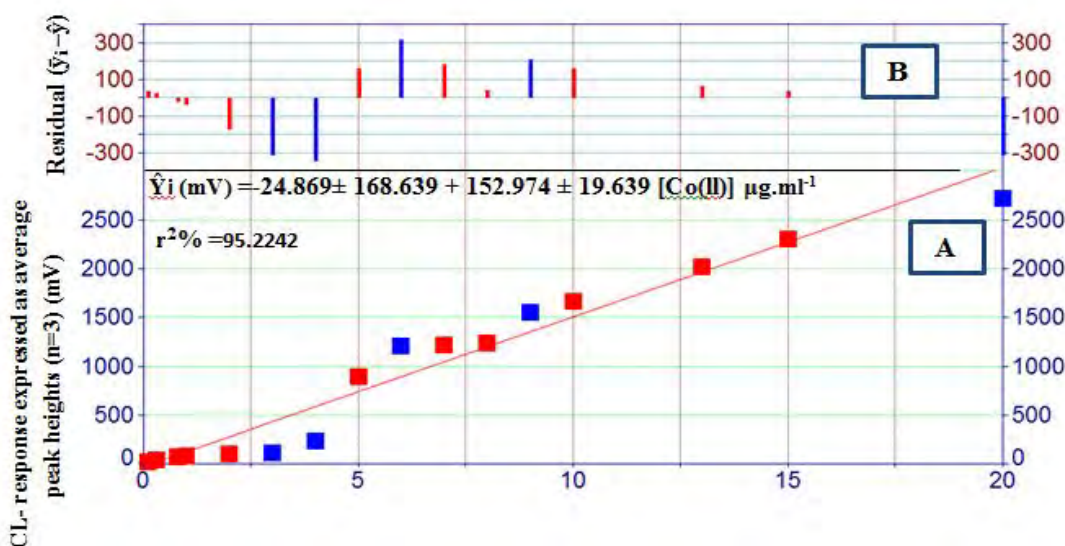
Figure 8- Calibration graph for the variation of Co (ll) concentration ($\mu g.ml^{-1}$) on: - A: CL- response expressed by linear equation, B- residual ($\bar{y}_i$– $\hat{Y}i$) , $\bar{y}_i$: practical value ,$\hat{Y}i$: estimated value.

Limit of detection (L. O. D)

Three different approaches were used, gradual dilution of lowest concentration in the calibration graph, detection based on the numerical value of slope or from the linear regression plot. Table 8 tabulated all these calculation value of detection limit for 40μL sample volume.

Table 8- Summery of limit of detection based on different approaches at 40 μL sample volume.

Practically based on gradual dilution for minimum Concentration	Based on the value of slope theoretical based on slop value X = 3S$_B$ / slope	Linear equation $\hat{Y}i$ (mV) = Y$_B$+3S$_B$
0.2000ng.	2.5600ng.	0.1608 μg.

S$_B$: standard deviation of blank solution repeated for 13 times. , X= value of L.O.D based on slope.
Y$_B$: average response for the blank solution (equivalent to intercept in straight line equation).

Repeatability

The repeatability of measurement was studied at three variable concentrations of Co (II) ion namely 1, 3, 5 µg.ml^{-1} at optimum parameters. The repeated measurements for five successive injections were measured and obtained results were tabulated in table. 9which shows that the percentage relative standard deviation was less than 2.5%, while figure 9 shows the CL-response -time profile for five successive repeatable measurements of Co (II) ion.

Table9- repeatability results of Co (II) ion at optimum parameters by CFIA-CL method.

[Co] µg.ml^{-1}	no. of injection	CL- response expressed as average peak height (mV)	Standard deviation σ_{n-1}	RSD %	Confidence interval of the mean at 95% $\bar{y}_i \pm t_{0.05/2,\ n-1}\ \sigma_{n-1}/\sqrt{n}$
1	5	269.2	3.347	1.2432	269.2 ± 4.156
3	5	729.6	6.229	0.8537	729.6 ± 7.734
5	5	1114.8	25.203	2.2608	1114.8 ± 31.288
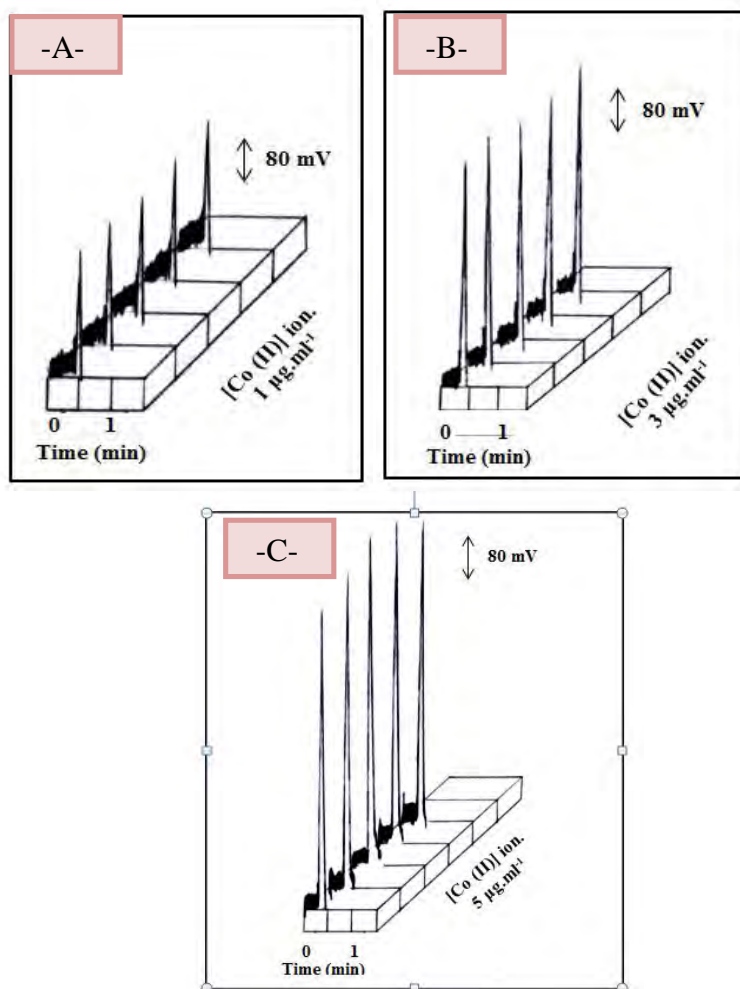
Figure 9- The CL-response -time profile for five successive repeatable measurements of Co(II) ion ; **A**- 1.0 µg. ml^{-1}, **B**- 3.0 µg. ml^{-1},**C**- 5.0 µg. ml^{-1}

Applications

The established method was used for the determination of Cobalt (II)ion in CoMo catalyst type (K F124-3E, AXSENCE-France). The standard addition method was applied by preparing a series of solutions via transferring 2 ml of catalyst dissolution product ($5\mu g.ml^{-1}$) to each of the nine volumetric flasks (100ml), followed by the addition of (0, 1, 2, 3, 4, 5, 8, 10, and 16 ml) from the standard solution of Cobalt (II) ion (100 $\mu g.ml^{-1}$) in order to have the concentration range from (0-16 $\mu g.ml^{-1}$) for the preparation of standard addition calibration plot. Results were mathematically treated for standard addition method and they are tabulated in table 10 and 11.

Table 10 -Summary of linear regression equation of estimating Co (II) ion by Luminol$_{G.B.}$- H$_2$O$_2$- Co(II) ion (standard addition method).

Range of Co (ll)ion conc. ($\mu g.ml^{-1}$)	No.of measure-ements (n)	Linear equation $\hat{Y}i$ (mV) = a ± ts$_a$ +b ± ts$_b$ [Co(ll)] $\mu g.ml^{-1}$ at confidence level 95% , n – 2	r , r^2%	$t_{(0.05/2),7}$ at 95% confidence limit	t_{cal} $t=\frac{\lvert r\rvert\ \sqrt{n-2}}{\sqrt{1-r^2}}$
0-16	9	$869.53 \pm 515.25 + 174.63 \pm 70.92 \times [X]$	0.9104, 82.889	2.365 < 5.8243	

$\hat{Y}i$ (mV) =Estimated CL-response for (n=3), [x] = [Co (II)] $\mu g.ml^{-1}$, r = correlation coefficient, r^2% = linearity percentage., t$_{tab=}$t$_{0.05/2 , n-2}$ at 95% confidence level.

Table11-Co (II) ion determination in CoMo catalyst type (K F124-3E) using Luminol$_{G.B.}$- H$_2$O$_2$- Co(ll) ion by standard addition method.

Type of sample	Wt. of sample (g.)	Wt. of CoO in sample (g.)	Wt. of Co(ll) ion in sample (g.)	[Co(ll)] $\mu g.ml^{-1}$	[Co(ll)] $\mu g.ml^{-1}$ after dilution 2.02ml/100 ml (Theoretically)	Average of CL-response (n=3), (mV)	[Co(ll)] $\mu g.ml^{-1}$ (practically)	Recovery %
CoMo catalyst (K F124-3E)	1.00	0.04	0.03146	247.4632	5.000	145.333	4.9793	99.60%

Conclusion.
A chemiluminescence – CFIA method is proposed for determination of Co(II) ion and its applied successfully in determination of cobalt (II) ion in CoMo catalyst type (K F124-3E). The method based on oxidation of luminol (CL-donor) by hydrogen peroxide in the presence of Co(II) ion as a catalyst metal ion for the CL- reaction . The proposed method is simple, rapid and sensitive.

References
1. Davis,J.R. **2000.** *ASM Specialty Handbook: Nickel, Cobalt, and their alloys*. ASM International, USA.
2. Sivasakthi, p. and Sathaiyan, N. **2012.** Cobalt recovery from waste catalysts (petroleum industry from Gujarat).*open journal of metal ,* 2, pp: 24-30.
3. Okomoto, Y. **2003.** Preparation and application of Co-Mo model sulfide catalysts for hydrosulfurization .*prepr.pap.-American Chemistry Society, Div.Fuel Chemistry,* 48, pp: 599-600.
4. Barik, S.P. Park, K.H.Parhi, P.K. Park, J.T. and Nam, C.W.**2012.**extraction of metal values from waste spent petroleum catalysts using acidic solutions. *Separation and Purification Technology,* 101, pp: 85-90.
5. Murata, S. and Nomura, M. **2004.** A novel oxidative desulfurization system for diesel fuel with molecular oxygen in the presence of Cobalt catalysts and aldehydes. *Energy fuels,* 18, pp: 116-121.
6. Hawkins, M.J. **1998.**Recovery of Cobalt from primary and secondary sources. *Journal of minerals, metals and materials society.*50, pp: 46-50.

7. Maroles, A. **1990.** Flame atomic absorption spectrometric determination of iron, nickel, cobalt and molybdenum in petroleum industry catalysts after microwave oven digestion. *Analytical Chemica Acta.,* 235, pp: 405-411.

8. Hajishaban, A.M. Dadfania, S.Dehghan,K . **2003.** On-line preconcentration and determination of Cobalt by chelating micro columns and flow injection atomic spectrometry.*Talanta* , 59, pp: 719-725.

9. Chen, J. Teo, K.**2001.**Determination of Cobalt and Nickel in water samples by flame atomic absorption spectrometry after cloud point extraction. *Analytical Chemica Acta. ,* 434, pp: 325-330.

10. Dadfarnia, S.Jafarzadeh, H. **1999.**On-line trace enrichment and determination of Cobalt ion as an anionic complex by flow injection atomic absorption spectrometry. *Microchemica Acta Journal,* 63, pp: 226-234.

11. Cador, S. Goi, R. Bacca, N. **2005.** Flame atomic absorption determination of Cobalt in water after extraction of its morpholinedithiocarbamatecomplex. *Journal Brazilian Chemistry Society,* 16, pp: 957-962.

12. Hasanpour, F.Teimori, H. Fouladgar, M. Taei,M. **2013 .**Trace and selective determination of Cobalt(ll) in water and salt samples using cathodic adsorption stripping voltammetry in the presence of pyrogallol red. *Journal .Serbian Chemistry Society,* 78, pp: 717-724.

13. Paleo logos, E. Prodromidis, M. Giokas, D. Karayannis, M. **2002.** Highly selective spectrophotometric determination of trace Cobalt and development of reagentless fiber-optic sensor. *Analytical Chimica Acta,* 467, pp: 205-215.

14. Bezarra, M. Santelli, R. **2007.** International standardization for the determination of Cadmium, Cobalt, Chromium and Manganese in saline water from petroleum industry by inductively coupled plasma optical emission spectrometry after cloud point extraction. *SpectrochemicaActa Part B:Atomic Spectroscopy ,* 62, pp:985-991.

15. Shakir,I.M.A. Turky,N.S. **2013.** Spectrophotometric- continues flow injection analysis for the determination of Co(ll) ion in river and alloy samples via the determination of 10,10-dimethyl 9,9-diacrydenium dinitrate salt-hydrogen peroxide in alkaline medium, *Journal of Karbalaa University,* 11, pp:244-257.

16. Sabel, C. Neureuther, J. Siemann, S. **2010.** A spectrophotometric method for the determination of Zinc, Copper, and Cobalt ions in metalloproteinase using Zincon. *Analytical Biochemistry*, 397, pp: 218-226.

17. Rodriguez, A.M. De Torres, A.G. Canopavon, J.M. **1998.**Simulteneous determination of Iron, Cobalt, Nickel and Copper by Uv-visible spectrophotometry with multivariate calibration. *Talanta,* 47, pp: 463-470.

18. Ferreira, S.L.C. De Jesus, D.S.**1996.** The spectrophotometric and derivative spectrophotometric determination of Cobalt in the presence of large amounts of Nickel using Br- PADAP. *Journal Brazilian Chemistry Society,* 7, pp: 109-114.

19. Creton,R. Jaffe,L.F. **2001.** Chemiluminescence. As a Tool in Biomedical Research. *Biological Techniques,* 31 (5) , pp: 1098-1105.

20. Lancaster, J.S. **1992.** Chemiluminescence detection in analytical chemistry. *Endeavour*, 16 (4), pp.: 194 – 200.

21. Shakir,I.M.A. Turky,N.S. **2012.** New developed analytical- cluminometric (sensitized) continuous flow injection analysis for determination of ciprofloxacin; application to pharmaceutical preparetions. *Journal of Al-Nahrain University,* 15, pp: 11-21.

22. Garcia, M.A. Baeyens, W.R.G. **2000.** Principles and recent analytical applications of Chemiluminescence . *Analusis,* 28, pp: 686-698.

23. Do deigne, C. Thunus, L. Lejeune, and R.**2000**.Chemiluminescence as diagnostic tool. Areview.*Talanta*, 51, pp: 415-439.

24. Nakahara, S.Yamada, S. **1982 .**Chemiluminescence for the determination of traces of Cobalt (II) by continuous flow and flow injection analysis. *Analytical Chimical Acta,* 141, pp: 255-262.

25. Lin, Q. Guiraum, A. Escobar, R. **1993.** Flow injection-Chemiluminescence determination of Cobalt (II) and Manganese (II). *Analytical Chimical Acta,* 283, pp: 379-385.

26. Cannizzaro, V. Bowie, A.R. Sax, A. Paul, J. **2000.** Determination of Cobalt and Iron in estuarine and coastal waters using flow injection with Chemiluminescence detection. *Analyst*, 125, pp: 51-57.

27. Song, Z. Wang, C. **2006.** Flow injection – Chemiluminescence determination of femtogram- level of Cobalt in egg yolk, fish tissue and human serum. *Food Chemistry,* 94, pp: 457-463.

28. Hirata, S. Hashimoto, Y. Alhara, M. Mallika, G.V. **1996.**On-line column pre-concentration for determination of Cobalt in sea water by flow injection-Chemiluminescence detection. *Fresenius journal Analytical Chemi*stry, 355, pp: 676-679.

29. Burr, J.G. **1985.** *Chemi. And Bioluminescence*, Marcel Dekker Inc., New York, U.S.A., p: 215-217