

# A Novel Instrumental Method for the Determination of Cobalt (II) ion using NAG-ADF-300-2 Analyser, via the Formation of a Precipitating Reaction Product Through On-Line Long Distance (300 mm) and Short Path Length (2 mm) Chasing of Sample Segment

Nagam Shakir Turkie Al-Awadi

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

## Abstract

A new instrument is presented for determination of Co (II) ion using precipitation reaction NAG-ADF-300 – 2 analyser is used for attenuation of incident light (white snow light emitting diode) at two stages, first one is 110 mm while the second one is 60 mm with a separation distance of 100 mm reaction of Co (II) ion with rubeanic acid in alkaline medium forms a black precipitate. The attenuation of this precipitate to the incident light is measured in a very repeatable, reproducible manner of RSD% less than 1% at variable concentrations. Line or calibration graph extend from 0.02 – 0.1 mmol / L Cobalt (II) ion. 30 sample / hr. can be handled. This instrument is easy to use and have extended ranged of working parameters. 50-500  $\mu$ L samples can be manipulated using 2- line system. Limit of detection (L.O.D) is 0.5 $\mu$ mol L<sup>-1</sup> at 50  $\mu$ L for cell A and 7  $\mu$ mol L<sup>-1</sup> at 200  $\mu$ L sample volume for cell B. The method was applied successfully for the determination of Co (II) ion in two different alloys.

**Key word:** Turbidometry, Flow injection analysis, Cobalt (II) Ion. and snow white light emitting diode.

## Introduction

Cobalt is a ferromagnetic metal with a specific gravity of 8.9. Pure cobalt is not found in nature, but compounds of cobalt are common small amounts of it are found in most rocks, soil, plants, and animals. It is found naturally only in chemically combined form. The free element, produced by reductive melting, is a hard, lustrous, silver-gray metal. Cobalt based blue pigments have been used since ancient times for jewelry and paints. And to impart a distinctive blue tint to glass .Cobalt is used in the preparation of magnetic, wear- resistant and high-strength alloys.

Cobalt silicate and Cobalt (II) aluminate (CoAl<sub>2</sub> O<sub>4</sub>.Cobalt blue) give a distinctive deep blue color to glass, small, ceramics, inks, paints and varnishes. Cobalt occurs naturally as only one stable isotope, Cobalt-59, Cobalt-60 is a commercially important radioisotope, used as a radioactive tracer and in the production of gamma rays. Cobalt is the active center of coenzymes called cobaltamins, the most common example of which is vitamin B<sub>12</sub>. As such it is an

essential trace dietary mineral for all animals [1]. Cobalt in inorganic form is also an active nutrient for bacteria, algae and fungi. Common oxidation states of cobalt include +2 and +3, although compounds with oxidation states ranging from -3 to +4 are also known .A common oxidation state for simple compounds is +2. Cobalt (II) salts form the red-pink [Co (H<sub>2</sub>O)<sub>6</sub>]<sup>+2</sup> complex in aqueous solution. Addition of chloride gives the intensely Blue [CoCl<sub>4</sub>]<sup>2-</sup> [2]. Several oxides of cobalt are known, green Cobalt (II) oxide (Co O) has rock salt structure.

It is readily oxidized with water and oxygen to brown Cobalt (III) hydroxide (Co (OH)<sub>3</sub>). At temperatures of 600- 700 C°, Co O oxidizes to the blue Cobalt (II, III) oxide (Co<sub>3</sub>O<sub>4</sub>), which has a spinel structure [3]. Black Cobalt (III) oxide (Co<sub>2</sub>O<sub>3</sub>) is also known Cobalt oxide are antiferromagnetic at low temperature: Co O (Neel temperature 291 K) and Co<sub>3</sub>O<sub>4</sub> (Neel temperature 40 K), which is analogous to magnetite Fe<sub>3</sub>O<sub>4</sub>, with a mixture of +2 and +3 oxidation states [4]. A good number of reviews have been made on the

use of large number of chromogenic reagents for the spectrophotometric determination of Cobalt [5, 9] are in various complex materials using isoamylxanthate with the use of surfactants in the presence to some metals, cyanex 923, 1-(2-pyridylazo) -2- naphthol in micellar, 3- (2-thiazolylazo)-2, 6-diaminopyridine and 10, 10 -dimethyl 9, 9-diacridinium dinitrate salt.

Number of published work [10, 14] dealt with a highly selective method such as chemiluminescence, fluorescence using continuous flow injection system. The present work is concerned with the determination of Cobalt (II) ion with rubeanic acid (or dithio-oxamide) in alkaline solution of sodium hydroxide which in turn gives a black precipitate. The concentration of cobalt (II) ion is measured according to the attenuation of the dark particulate to incident light at two detecting flow cells that have the same input and output with a distance of 100 mm in between the two cells to allow either completion of reaction then followed by detection at the second detecting stage.

## Materials and Methods

### Chemicals

All chemicals used were of analytical reagent grade. Distilled water was used to prepare all the solutions. Freshly prepared solutions were always used. Standard solution (w/v) of rubeanic acid (dithio- oxamide)  $(CS.NH_2)_2$ ,  $120.20 \text{ g.mol}^{-1}$ , BDH,  $10 \text{ mmol.L}^{-1}$  was prepared by dissolving  $0.1202 \text{ g}$  of the reagent in  $0.1 \text{ mol / L}$  solution of NaOH and diluting to the mark with the same in a  $100 \text{ ml}$  calibrated flask to give a stock solution, which was diluted further as required. A standard solution of  $10 \text{ mmol / L}$  Cobalt (II) ion as  $Co(NO_3)_2.6H_2O$  ( $291.03 \text{ g.mol}^{-1}$ , BDH) was prepared by dissolving  $0.72757 \text{ g}$  in  $250 \text{ ml}$  distilled water.

Hydrochloric acid,  $1 \text{ mol.L}^{-1}$ . Dilute  $44.19 \text{ ml}$  of  $35\% \text{ HCl}$  (sp.gr.  $1.18 \text{ g.ml}^{-1}$ , BDH) with water in a  $500 \text{ ml}$  (Standardized with standard  $Na_2CO_3$  solution). A stock solution of sodium carbonate  $Na_2CO_3$  ( $50 \text{ mmol/L}$ ) ( $105.97 \text{ g.mol}^{-1}$ , BDH), prepared by dissolving  $2.6493 \text{ g}$  in  $500 \text{ ml}$  distilled water. A stock solution of sodium hydroxide NaOH ( $0.5 \text{ mol/L}$  (After Standardized with HCl solution) ( $40 \text{ g.mol}^{-1}$ , BDH), prepared by dissolving  $5.00 \text{ g}$  in  $250 \text{ ml}$  distilled water.

### Washing Buffer [15]

A washing buffer solution containing  $40 \text{ g}$  EDTA (disodium salt),  $7 \text{ g}$  of Ammonium chloride and  $57 \text{ ml}$  of  $25\% \text{ (V/V)}$  ammonia, was prepared by dissolving the chemicals in succession in a total volume of  $500 \text{ ml}$  of distilled water followed by dilution to  $1 \text{ L}$  in a volumetric flask.

### Sample Preparation

Two kinds were used for determination of cobalt (II) ion in alloys. First: Using high purity iron alloys B.C.S.No.260/2 contain  $0.009\% \text{ Co (II)}$ . Second: high purity iron alloy as granules B.C.S .No 149/2 and contain  $0.012\% \text{ Co (II)}$ . Two grams of each alloy were weighted into a separate  $400 \text{ ml}$  beakers containing  $50 \text{ ml}$  of  $HNO_3:HCl (1:1)$ .

The content is heated with constant stirring until  $NO_2$  brown fumes is ceased. The resulted solution is diluted to  $100 \text{ ml}$ , filtered and the filter paper is washed many times quantitatively. The resultant solution is collected into  $100 \text{ ml}$  volumetric flask and completed to the mark with D.W; from which a series of cobalt (II) ion is prepared for further study.

### Apparatus and Design of NAG-ADF-300-2 Analyser:

#### Apparatus

A peristaltic pump: four channel, variable speed (Ismatec, Switzerland), 6-port medium pressure injection valve (IDEX corporation, USA) with a sample loop ( $1 \text{ mm i.d.}$ , Teflon, variable lengths) used for injection of various sample volumes. All responses were measured by NAG – ADF-300-2 Analyser (homemade) by using Snow White Light Emitting Diode (SWLED) as a source with a solar cell as detection unite. The output signals were recorded by potentiometric recorder Y (Z) –t(d) – Two pens recorder - Siemens, Germany, range ( $1-500 \text{ mV}$  or  $1-500 \text{ Volt}$ ).

#### Y- Junction Point

Homemade liquid junction point piece made of Poly Methyl Methacrylate (PMMA) for the mixing of chemical reactants in reaction manifold, which contain one outlet and two inlet in the form of Y-junction. Mixing coil:

Variable glass tube lengths with I.D  $2 \text{ mm}$  and outside diameter of  $4 \text{ mm}$  were used as a mixing coil, delay and for completion of reaction.

## Design of Long Distance Chasing Photometer for 300 mm Length (NAG – ADF-300-2) Analyser & Methodology

The NAG-ADF-300-2 is a unique instrument made at home; which represent a flow cell of 300mm length and a path length of 2mm. The symbols of ADF represent the attenuation, Divergence and the Fluorescence. The instrument is of three compartments; two of them is a full equipped separate instrument of eleven and six sources of irradiation. The sources are a White Snow Light Emitting Diode symbolized by WSLED. The two compartments are separated by 100 mm unguarded regions.

The instrument offers a separate measurement of each single cell unite for attenuation as well as diverged and/or fluorescence light that is either remained unabsorbed or lost due to impact of incident photons at 0-180° as it is the case in the attenuation measurements or diverged light that can be measured at 0-90°. Mixing or combining any of the released responses from either cells (designed as cell No.1 i.e.; cell A or cell No.2; cell B) can be recorded. Figure no.1 shows structural composition of the instrument core. Also the figure shows that the detection unit is made of twin solar cells

of 110mm length that covers the unit A; while a 55mm length solar cell cover up the second unit cell B. The detection range of the solar cell is 410nm to 1150nm.

A selector control knob of four variable light intensity that can be applied as request according to variable optimization of reaction parameters for any specific reaction. Colloidal as well as crystalline precipitated particulate can be handled and dealt with. The reaction of rubeanic acid with Cobalt (II) ion gives a black precipitate in alkaline medium [16] as shown below. This reaction was used to asses Cobalt (II) in alloys. Figure No.2 shows a flow gram of the manifold used for this determination. A two lines system was used.

The first line is the carrier (distilled water stream line; while the second one is reagent line Rubeanic acid solution. Both line meet at a junction point .Figure No.3.shows kind of responses for a sample volume of 115µL Cobalt (II) ion (0.1mmol/L) instantaneous response of both cells (cell A& cell B) using maximum irradiation intensity. Figure no 4: y (z)-tpotentiometric recorder output showing various the scan speed y (z) – t (d) from 60 Sec / 10 mm to 5 sec / 10 mm.

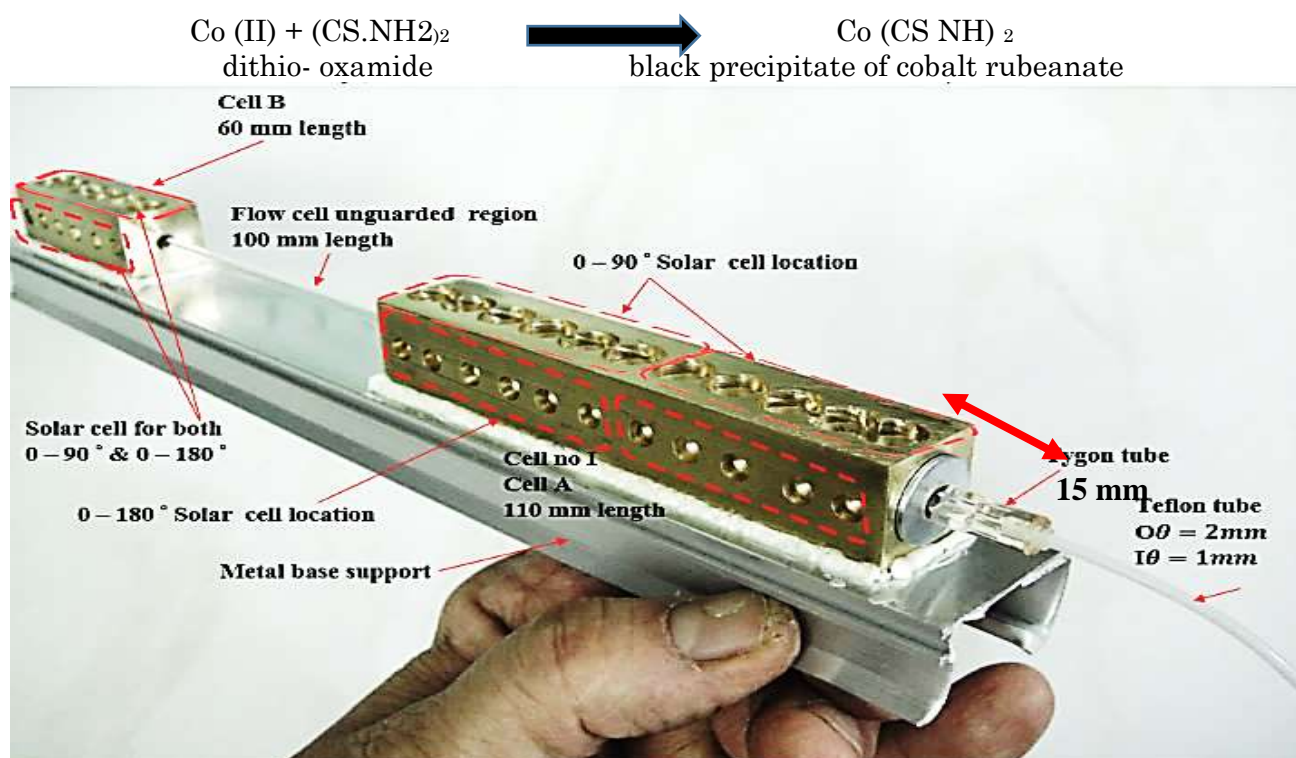


Figure 1: The core structure of the ISNAG-ADF-300-2; showing various locations of WSLED, Detectors and the flow cells .Also the unguarded region of 100 mm length

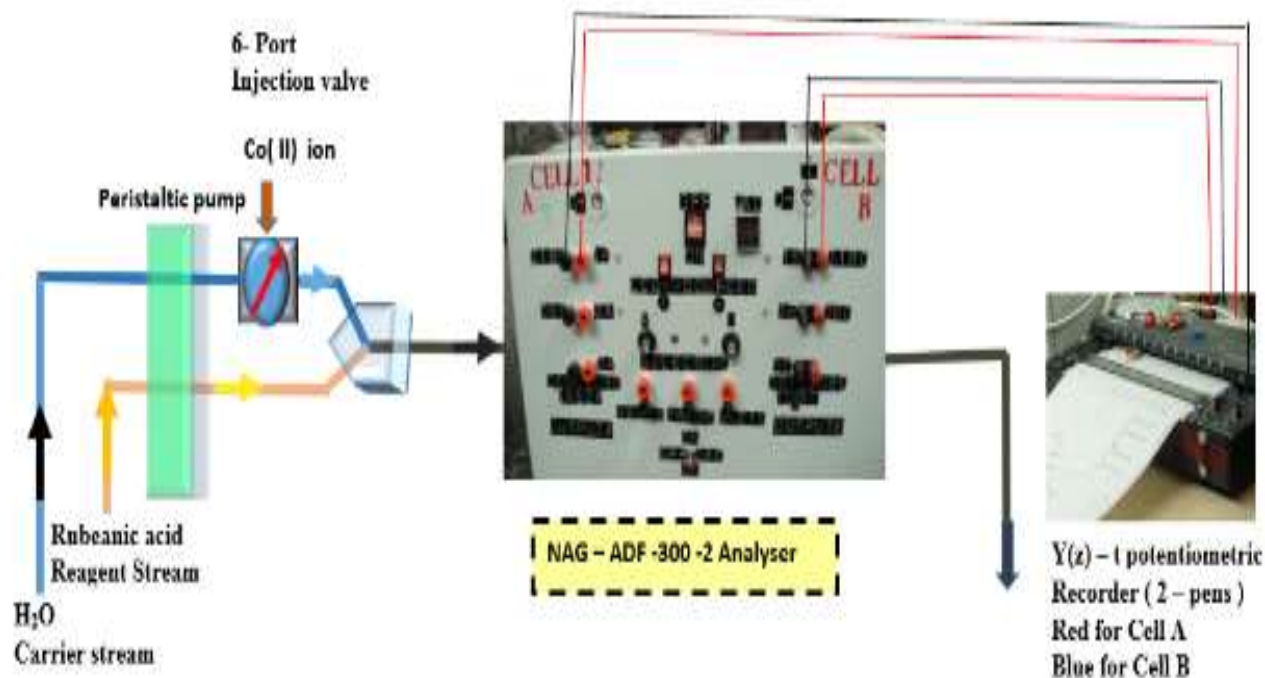


Fig NO. 2 : Manifold flow gram for the determination of Cobalt (II) ion , showing the complete setup .

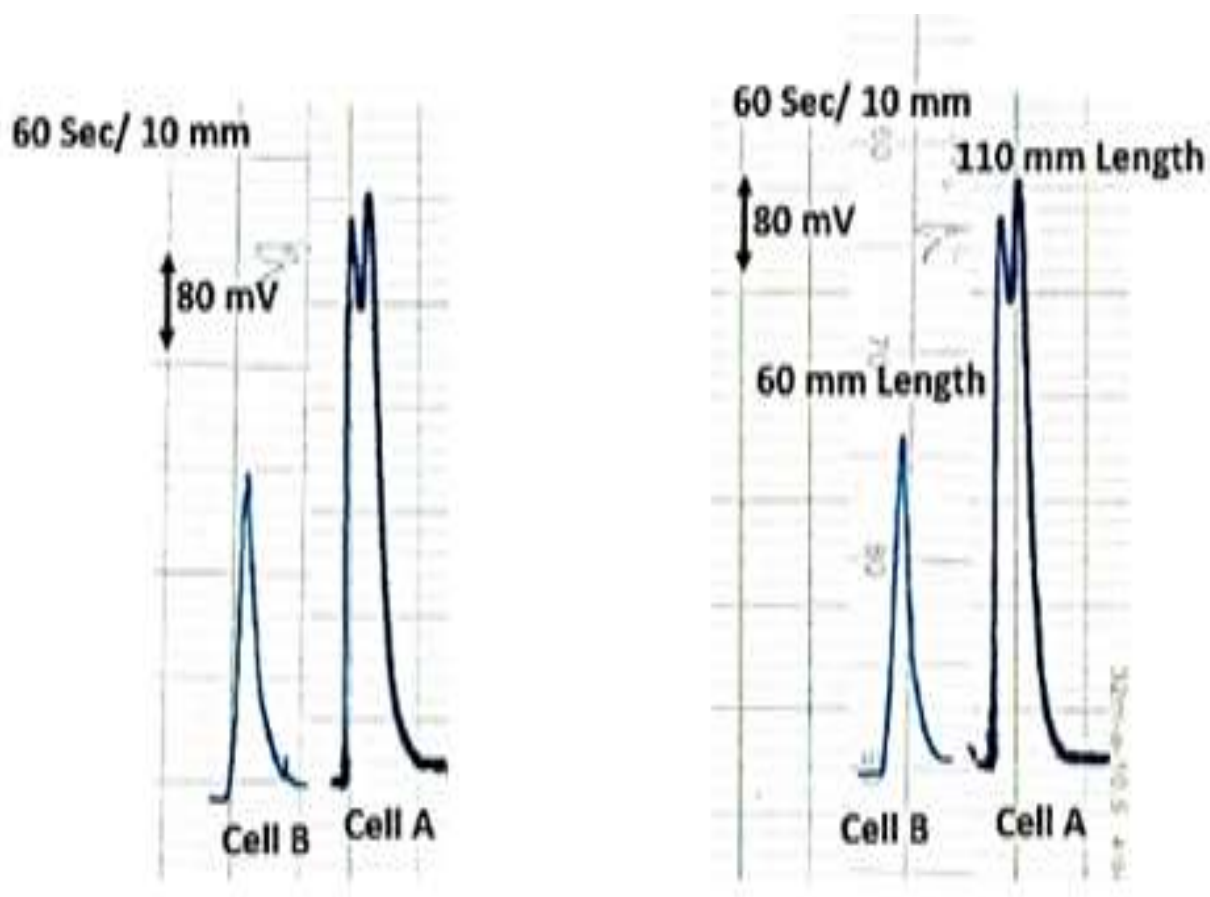


Figure 3: Attenuation of the incident light of both cells A and B. Selection of incident light is on maximum ( i. e ; I= 4 ) . No external delay reaction coil. Sample volume 115  $\mu$ l, flow rate 2.25 ml/min. Co (II) ion 0.1 m mol/L. Usually there is a time lag between the responses of both cells



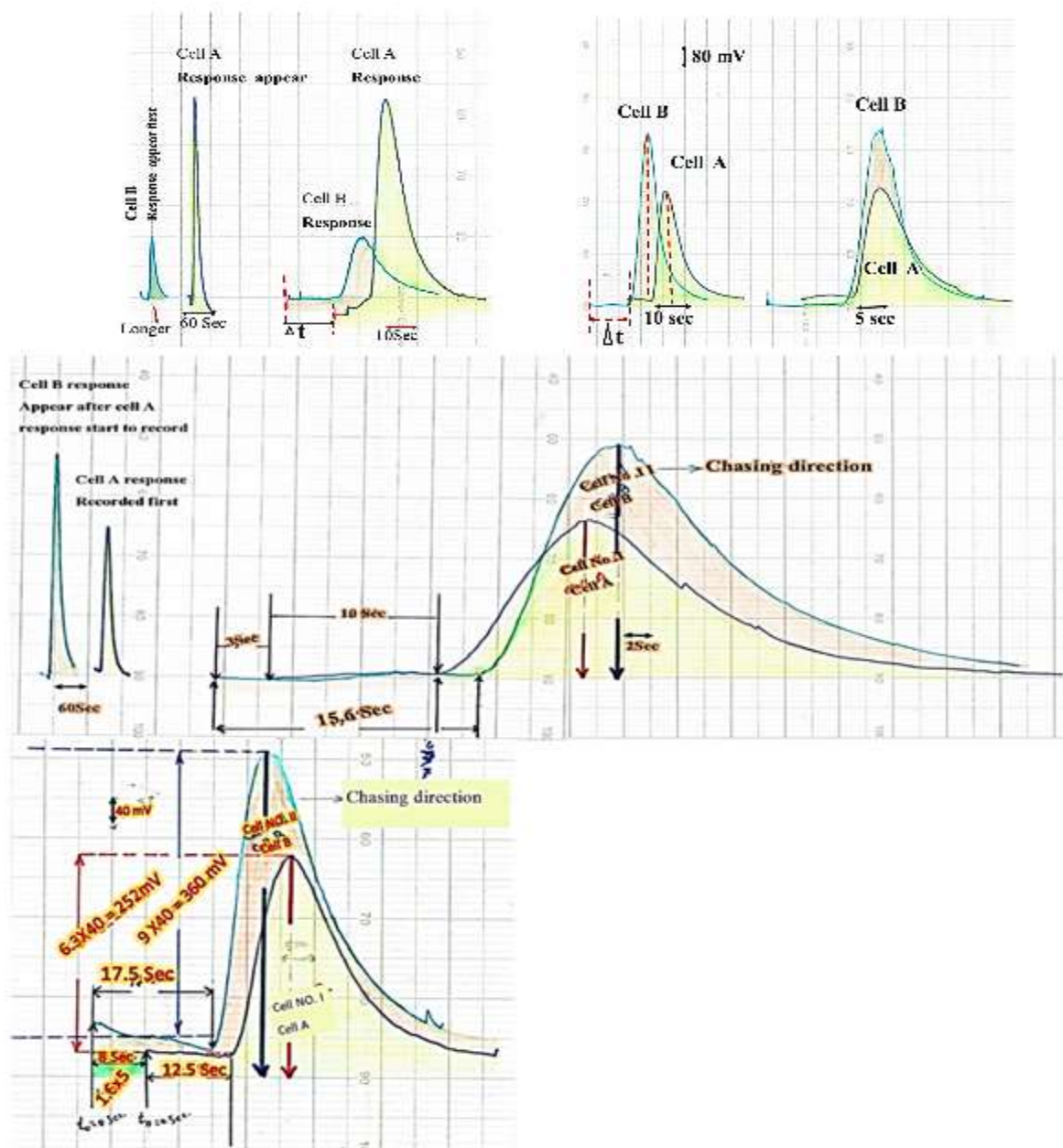


Figure 4: y (z) – t recorder potentiometric output showing variable scan speed from 60 Sec / 10 mm to 5 sec / 10 mm. Varying the order of appearance of cell A response relative to cell B response (as required or for analyst convenient)

## Results and Discussion

### Effect of Variable Light Intensity on Attenuation Response of Cell A and Cell B

An experiment was conducted to study the effect of light intensity  $P_0$  on the attenuation of light process while travelling through 2mm path length and a total distance of 270mm.length. The first 110mm is for cell A while the last 60mm.is for cell B. Four degrees of intensities were used. Figure No. 5 shows the output responses of both cells (A and B) recorded instantly for an intensity of maximum (i.e.; 4). It shows that at high intensity cell A gave high response while the

optimum intensity for cell B is  $P_0=3$  for 115 $\mu$ L of 0.1mmol/L of Co (II) ion and 100 $\mu$ M of Rubenic acid ( optimum concentration that was used for further experiments as shown in Figure No.5 and table No.1) at 2.25ml./min flow rate.

The total results obtained were tabulated in Table No. 2 and shown in Figure No.6. This experiment was followed by another experiment using fixed light intensity (in this case  $P_0=4$ ) but using different flow rate of 1, 2.25, 3.25 and 4.25 ml /min. Figure No.7 and Table No. 3 shows and indicate that at low flow rate there is an increase in the attenuation of incident light for cell B While

an increase of height profile at high flow rate for cell B.

In each study that there were superior responses of cell A compared with the responses obtained for cell B. Those above two experiments were followed by another experiment using repeated parameters as above but at a lower light intensity (in this case  $P_0=3$ ). Figure No.7 indicates that high responses with clear S/N signal is obtainable.

A conclusion that can be drawn that a light intensity of 4 can be used comfortably for cell A while a light intensity of 3 can be used for cell B. High light intensity is required for a dense bulky precipitate while a dispersed low density precipitate can prefer low light intensity. As the precipitate in its first formation is more likely a small particulate with large Q-S/S (Van viemer equation - Q: total concentration of salt, S: molar solubility) forming a dense bulky precipitate; while in the case of cell B agglomerate of the precipitate might be dispersed by long distance that the precipitate travels which causes in giving enough time to solubilize some of the precipitated particles.

Further experiment was carried out to create an environment of delaying the reach of the precipitate to cell A in a condition similar to cell B as it receives the formed precipitate after 210mm distance.

Figure no.8 and table no. 4, shows a very improved signal can be obtained and a delay reaction coil is quite necessary to use the cell A for the determination of Co (II) ion. This of course is not supposed to be the case in every conducted reaction ; Using the optimum flow rate with a various volumes (50-200  $\mu\text{L}$  ) were injected using open valve mode i.e. by allowing enough time for the purge up sample segment concentration and volume from the sample loop in the injection valve.

The data obtained were plotted as shown in Fig. No. 9 and Table no.5 showing that the optimum sample volume for cell A is 50  $\mu\text{L}$  for better response, while increasing sample volume more than 50  $\mu\text{L}$  gave broadening of the signal base ( $\Delta t_B$ ) as well as the peak maxima which was most probably attributed to continuous long time duration of colour segment in front of detector, while cell B prefer larger sample volume (here its 200  $\mu\text{L}$ ).

**Table No.1: Variation of the rubeanic acid concentration on attenuation of incident light (turbidity) Using rubeanic acid - Co (II) (0.1 mmol.L<sup>-1</sup>) in base medium, with sample volume 115 $\mu\text{L}$ , flow rate: 2.25ml.min<sup>-1</sup> intensity of light ( $P_0=4$ )**

[Rubeanic acid] mmol/L	Attenuation of incident light $T_{(0-180^\circ)}$ expressed as an average peak heights (n=3) $\bar{y}_i$ (mV) and confidence interval of the average response (at 95% confidence level) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1}/\sqrt{n}$	
	Cell A	Cell B
0.005	552 $\pm$ 1.23	80 $\pm$ 1.65
0.01	1090 $\pm$ 0.23	183 $\pm$ 1.32
0.05	1185 $\pm$ 0.89	256 $\pm$ 0.65
0.1	1200 $\pm$ 2.34	530 $\pm$ 1.33

**Table 2: Effect of intensity on the attenuation of incident light (turbidity) Using rubeanic acid (0.1 mmol/L) - Co (II) (0.1 mmol.L<sup>-1</sup>) in base medium, with sample volume 115 $\mu\text{L}$ , flow rate: 2.25ml.min<sup>-1</sup>**

Intensity of incident light ( $P_0$ )	Attenuation of incident light $T_{(0-180^\circ)}$ expressed as an average peak heights (n=3) $\bar{y}_i$ (mV) and confidence interval of the average response (at 95% confidence level), $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1}/\sqrt{n}$	
	Cell A	Cell B
1	396 $\pm$ 1.45	650 $\pm$ 2.43
2	480 $\pm$ 1.45	744 $\pm$ 2.34
3	696 $\pm$ 1.98	800 $\pm$ 1.34
4	1190 $\pm$ 1.94	256 $\pm$ 2.32

**Table No.3: Effect of flow rate (two lines streams) on the attenuation of incident light (turbidity) Using rubeanic acid (0.1 mmol/L) - Co (II) (0.1 mmol.L<sup>-1</sup>) in base medium, with sample volume 115 $\mu\text{L}$**

Flow rate (mL/min)	Attenuation of incident light $T_{(0-180^\circ)}$ expressed as an average peak heights (n=3) $\bar{y}_i$ (mV) and confidence interval of the average response (at 95% confidence level), $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1}/\sqrt{n}$	
	Cell A	Cell B
1	1080 $\pm$ 1.34	256 $\pm$ 1.56
2.25	1190 $\pm$ 1.45	800 $\pm$ 1.69
3.25	1200 $\pm$ 1.36	950 $\pm$ 2.54
4.25	1210 $\pm$ 1.54	980 $\pm$ 2.54

Table No.4: Effect of coil length on the attenuation of incident light (turbidity) Using rubeanic acid ( 0.1 mmol/L ) - Co(II) (0.1 mmol.L-1)in base medium , with sample volume 115 $\mu$ L,

Coil Length ( cm )	Coil Size $\mu$ L	Attenuation of incident light $T_{(0-180^\circ)}$ expressed as an average peak heights (n=3) $\bar{y}_i$ (mV) and confidence interval of the average response ( at 95% confidence level), $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1}/\sqrt{n}$	
		Cell A	Cell B
No coil	No coil	1190 $\pm$ 1.30	950 $\pm$ 0.89
9.5	300	1250 $\pm$ 0.45	830 $\pm$ 1.22
12.7	400	1180 $\pm$ 0.45	600 $\pm$ 0.95
15.9	500	1179 $\pm$ 0.98	350 $\pm$ 0.98

Table No.5: Effect of Sample volume on the attenuation of incident light (turbidity) Using rubeanic acid (0.1 mmol/L) - Co (II) (0.1 mmol.L-1) in base medium

length of sample loop(cm), i.d = 1mm	Sample volume ( $\mu$ L )*	Attenuation of incident light $T_{(0-180^\circ)}$ expressed as an average peak heights (n=3) $\bar{y}_i$ (mV) and confidence interval of the average response ( at 95% confidence level), $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1}/\sqrt{n}$	
		Cell A	Cell B
6.4	50	1300* $\pm$ 1.34	285 $\pm$ 1.43
9.6	75	1290** $\pm$ 1.67	800 $\pm$ 1.47
14.7	115	1250 $\pm$ 1.23	950 $\pm$ 2.49
25.5	200	1100 $\pm$ 2.64	1180 $\pm$ 2.69

\*: Sharp of profile \*\*: Broad of peak maxima \*: assumption is made that it is a cylinder

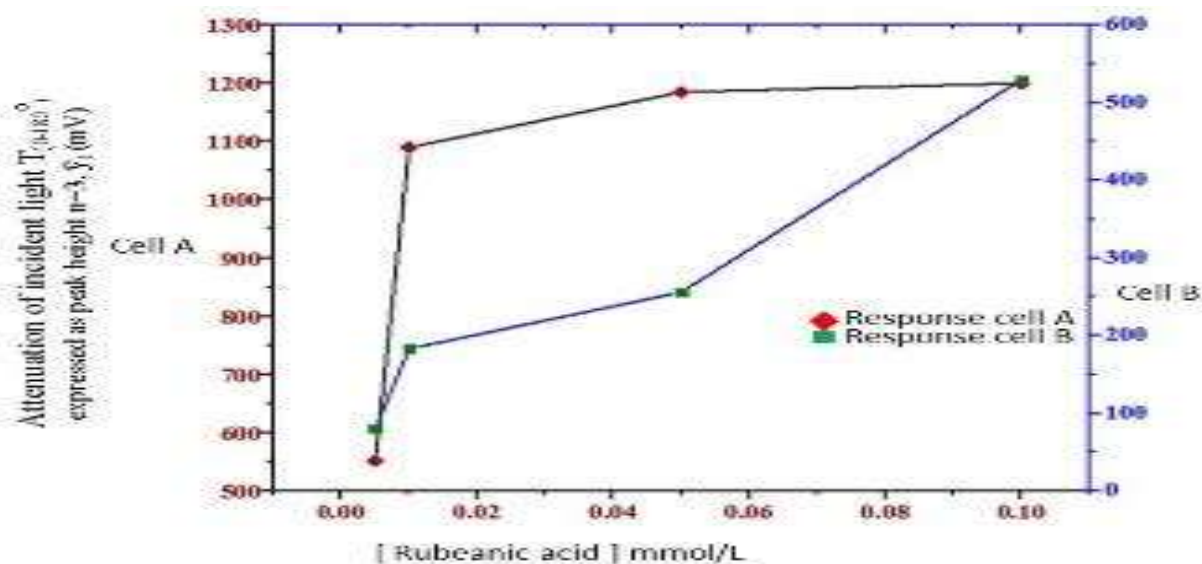


Figure (5) : Effect of Rubeanic acid concentration on Attenuation of incident light using Cell A and Cell B

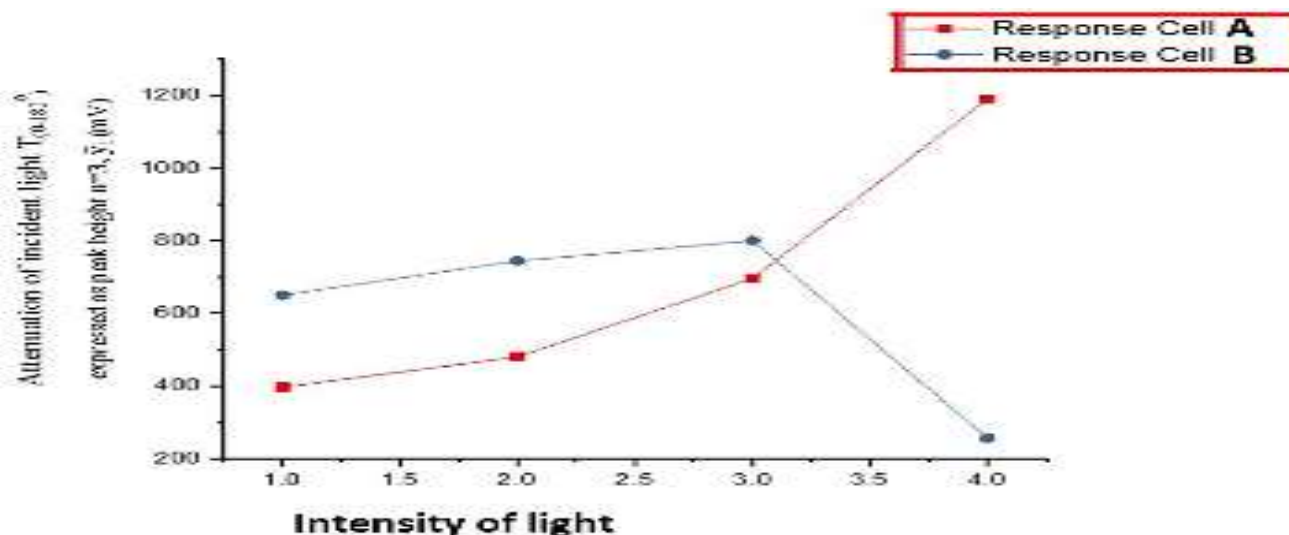


Figure 6 : Effect of intensity of light on attenuation of incident light usig cell A and Cell B .

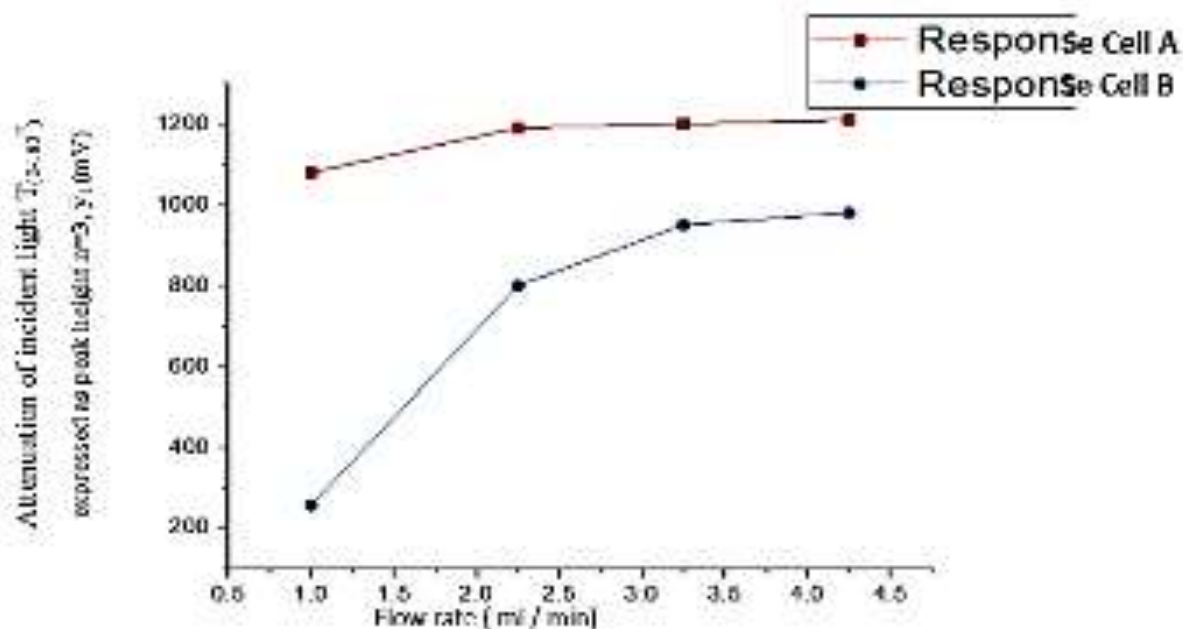


Fig. 7: Effect of flow rate on attenuation of incident light, Using parameter: Rubeanic acid (0.1 mmol.L-1)-Co (II) (0.1 mmol.L-1) for both Cell A and Cell B

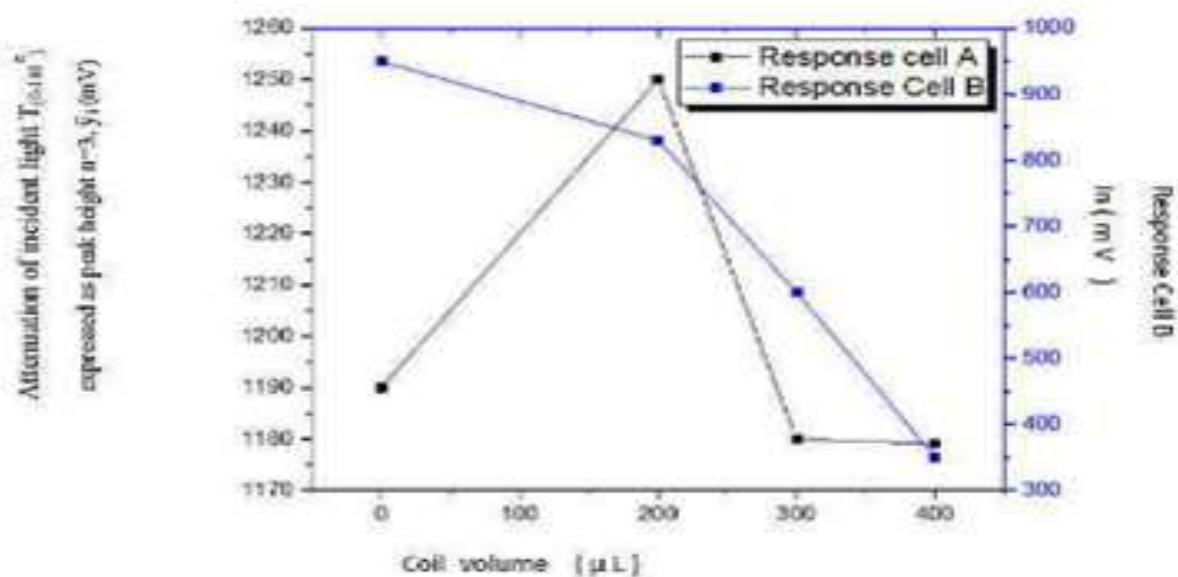


Fig. 8: Effect of Mixing coil on attenuation of incident light, Using parameter: Rubeanic acid (0.1 mmol.L-1)-Co (II) (0.1 mmol.L-1) for both Cell A and Cell B

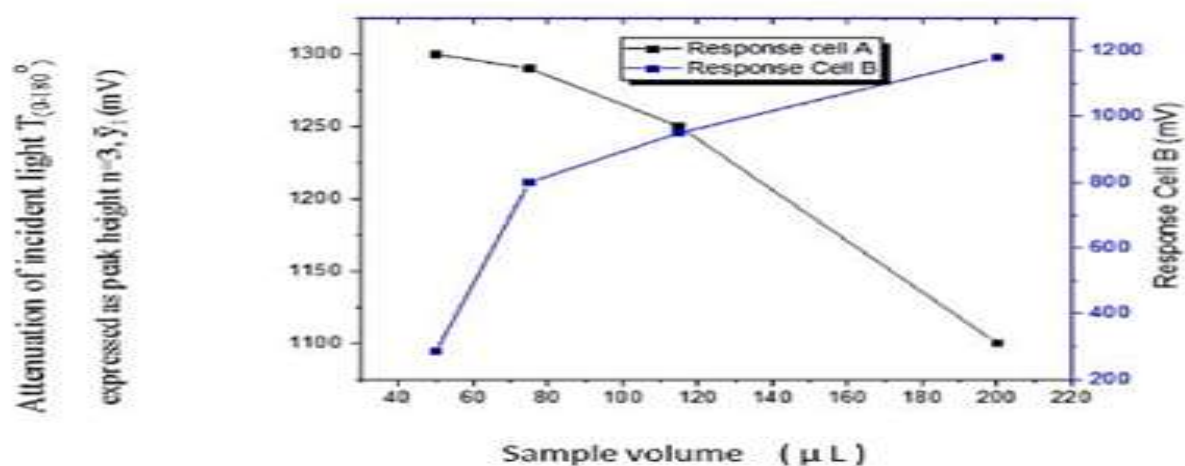


Fig. 8: Effect of sample volume on attenuation of incident light, Using parameter: Rubeanic acid (0.1 mmol.L-1)-Co (II) (0.1 mmol.L-1) for both Cell A and Cell B



### Scatter Plot for the Variation of Responses of NAG-ADF-300-2 Analyser for the Determination of Cobalt (II) ion in a Precipitation Reaction with rubeanic Acid in Alkaline Medium to form a Black Precipitate

According to the established conditional parameters that were studied in previous sections. An outcome of the physical parameters indicate that it is not necessary to use identical parameters in obtaining an acceptable sensitivity with good linearity and a better mathematical equation that can express most of the scatter point results leading to the calibration graph. Figure No. 9-A and 10-A shows the linear range of the calibration graph obtained for both cells (i.e.;

cell A and cell B respectively) after being extracted from scatter plots of both cells responses obtained using Y (Z)-t (d) potentiometric recorder. Table No.6 tabulate all the results obtained ( i.e.; correlation coefficient, Coefficient of determination, %squared capital  $R^2$ , slope, intercept and equations representing the dependent variable Y(Z) in mV, and the independent variable i.e.; Cobalt (II) ion concentration in mM ). Another mathematical treatment was conducted that an application of Savitzky-Golay [17] smoothed data filtering treatment was applied for each mathematically best fit linear regression equation [18-20]. The plot is shown in Figure No.9-B for Cell A ; while Figure No.10-B shows the same treatments for Cell B. Both can be used with no restriction at all.

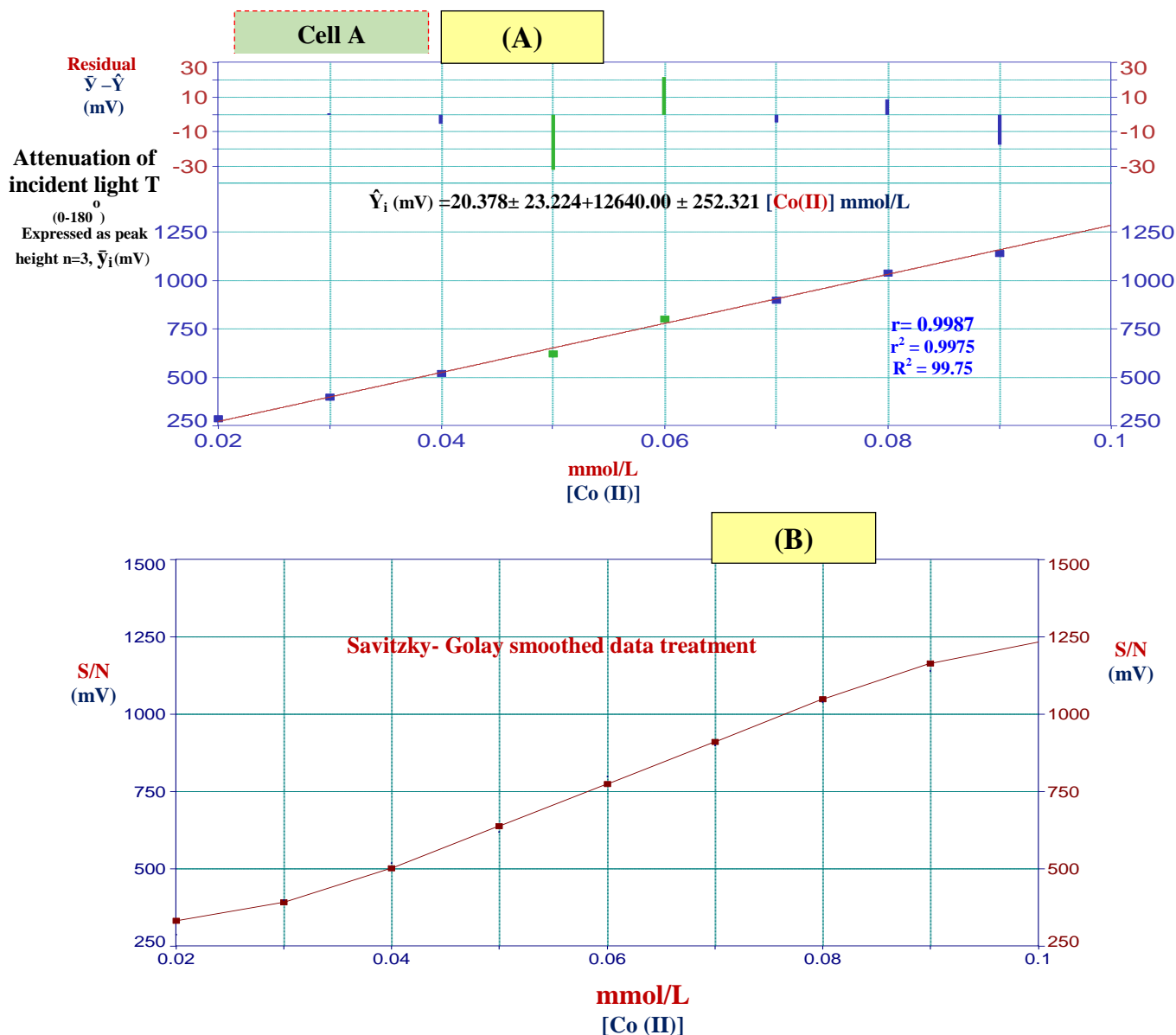


Figure 9: A- Linear calibration graph representing S/N responses in mV versus concentration of Co (II) ion in mM,  $R = 0.99872$ , Attenuated signal (mV) =  $20.38 + 1264 [\text{Co (II)}] \text{ mmol/ L}$ . B-SAVITZKY – GOLAY smoothed data treatment of the linear calibration graph for cell A

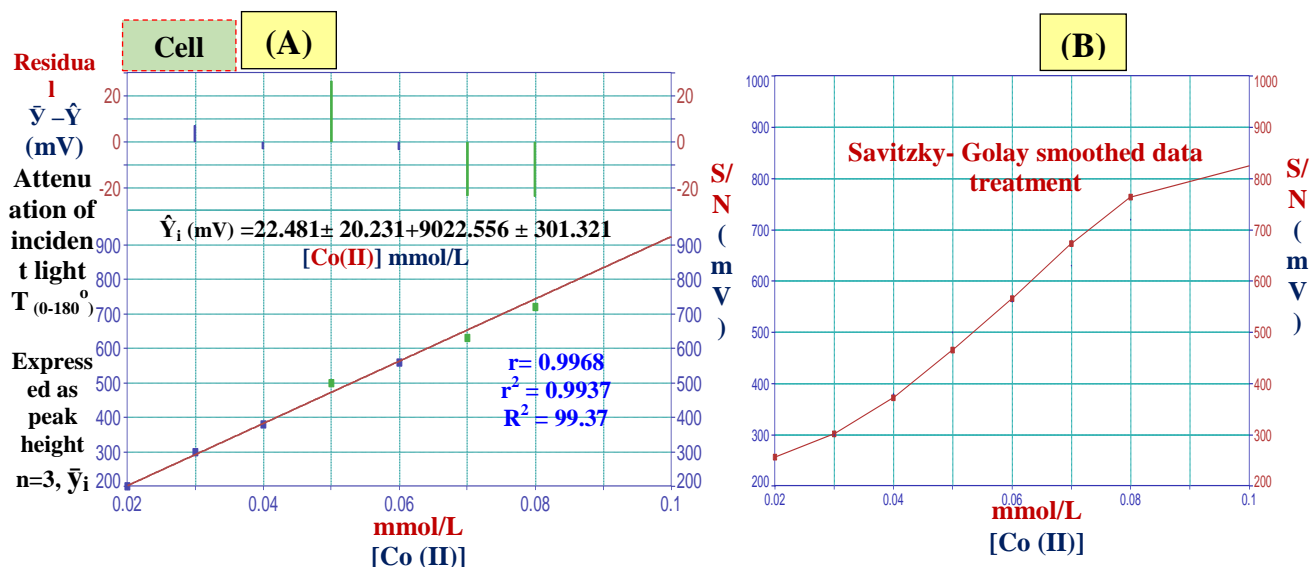


Figure 10: A- Linear calibration graph representing S/N responses expressed in mV versus concentration of Co (II) ion in mM,  $R = 0.99683$ , Attenuated signal ( mV)= 22.481+ 9022.556 [Co (II) ] mmol/ L . B - SAVITZKY – GOLAY smoothed data filtering treatment of the linear calibration graph for cell B

Table No. 6 -Summary of calibration graph results for the determination of Co (II) ion by Rubeanic acid - Co (II) ion

Linear dynamic range (mmol/L )	Linear equation $\hat{Y}_i \text{ (S/N) (mV)} = a \pm ts_a + b \pm ts_b [\text{Co(II)}] \text{ mmol/L}$ , at confidence level 95% ( $\alpha = 0.05$ , $n - 2$ ) two tailed	r	$r^2$	$R^2 \%$	a	b
	Cell A (n = 9)					
	Cell B (n = 8)					
0.02-0.1	$S/N(\text{mV}) = 20.38 + 12640[\text{Co(II)}]\text{mM}$	0.99872	0.99745	99.75%	20.38	12640.0
	$S/N(\text{mV}) = 22.48 + 9022.56 [\text{Co(II)}]\text{mM}$	0.99683	0.99367	99.37 %	22.48	9022.56

$\hat{Y}_i \text{ (mV)}$  = Estimated value for (n=3),  $[x] = [\text{Co (II)}] \text{ mM}$ ,  $r$  = correlation coefficient,  $r^2$ : coefficient of determination,  $R^2\%$ : % Capital R-square,  $a$ : intercept,  $b$ : slope

The limit of detection of Co(II) ion via successive gradual dilution of the minimum concentration in the linear range was  $0.5 \mu\text{mol L}^{-1}$  ( 1.475 ng / sample ) for cell A at  $50 \mu\text{L}$  sample volume while for cell B was  $7 \mu\text{mol L}^{-1}$  ( 82.6 ng / sample ) at  $200 \mu\text{L}$  sample volume. The repeatability of measurement was studied

at two concentrations of Co (II) ion 0.04 & 0.08 mmol/L at optimum parameters. The repeated measurements for six successive injections were measured and obtained results were tabulated in Table No. 7 which shows that the percentage relative standard deviation was less than 1%, for either cell A or cell B.

Table No.7- Repeatability results of Co (II) ion at optimum parameters by NAG – ADF-300-2 Analyser for  $n = 6$ ,  $t_{0.05/2, 5} = 2.57$

[Co(II) ] mmol/L	Attenuation of incident light $T_{(0-180^\circ)}$ expressed as an average peak heights (n=3) $\bar{y}_i \text{ (mV)}$ and confidence interval of the average response (at 95% confidence level) $\bar{y}_i \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$	RSD %
0.04	$520 \pm 2.57$	0.47
0.08	$1040 \pm 2.67$	0.24
0.04	$380 \pm 3.90$	0.98
0.08	$720 \pm 3.23$	0.43

## Applications

The established method was used for the determination of Cobalt (II) ion in two different alloys using cell A and cell B . The standard addition method was applied by preparing a series of solutions via transferring 8ml of 0.03051 mmol/L for high purity iron alloy ( B.C.S.No.260/2 – 0.009% Co(II) ion) to obtain 0.024406mmol/L to each

of the five volumetric flasks (10ml), followed by the addition of (0, 0.02, 0.025 ,0.03 & 0.035 ml) from the standard solution of Cobalt (II) ion (0.01 mmol/L ) in order to have the concentration range from (0-0.035mmol/L) for the preparation of standard addition calibration plot. While transferring 8ml of 0.04068 mmol/L for high purity iron alloy as granules (B.C.S.No.149/2 – 0.012%

Co (II) ion) to obtain 0.03254 mmol/L to each of the five volumetric flasks (10ml), followed by the addition of (0, 0.05, 0.06, 0.07 & 0.08 ml) from the standard solution of Cobalt (II) ion (0.01 mmol/L) in order to have the

concentration range from (0-0.08mmol/L). Results were mathematically treated for standard addition method and they are tabulated in Table 10 and 11.

**Table No.8 -Summary of linear regression equation of estimating Co (II) ion by Rubeanic acid - Co (II) ion (standard addition method)**

Type of alloy (Name, No. and content %)	Range of Co (II) ion conc. (mmol/L)	(n)	Linear equation $\hat{Y}_i \text{ (mV)} = a \pm ts_a + b \pm ts_b \text{ [Co(II)]mmol/L}$  at confidence level 95% , n – 2	r , r <sup>2</sup> %	B.C.S.No.260/2				
					B.C.S .No 149/2				
					Vol of 0.01Mm Co(II)ion (ml)				
					0	0.02	0.025	0.03	0.035
					0	0.05	0.06	0.07	0.08
					Conc. Of Co(II)ion (mmol/L)				
					0	0.02	0.025	0.03	0.035
					0	0.05	0.06	0.07	0.08
high purity iron alloy B.C.S.No.260/2 0.009%	0-0.035	5	CELL A -		RESPONSE (mV)				
			CELL B -		RESPONSE (mV)				
			264.658±32.430+10924.658±340,122[X]		0.99985 99.97%	265	485	535	590
122.877±67.212+4832.311±110.102 [X]			0.9943 98.87%	118	200	230	258	290	
242.577±98.341 + 7835.052± 179.542 [X]			0.9983 99.66%	240	630	720	810	850	
149.690 ±28.320 + 4159.974± 150.542 [X]			0.9845 96.92%	135	390	410	440	455	
high purity iron alloy as granules B.C.S .No 149/2 0.012%	0 – 0.08								

$\hat{Y}_i$  (mV) =Estimated value (n=3), [x] = [Co (II)] mmol/L ,n: No .of measurements , r = correlation coefficient , r<sup>2</sup> : coefficient of determination, R<sup>2</sup>% : % Capital R- square , a: intercept , b : slope

**Table No. 9: Co (II) ion determination in different using Rubeanic acid - Co (II) ion by standard addition method**

Type of sample	Wt. of sample (g.)	Wt. of Co (II) in 2 g of sample	Wt. of Co(II) ion in sample theoretically	[Co(II)] practically	Wt of [Co(II)] ) In 2 g 100 g	% of Co (II) ion Practically	Recovery %
CELL A							
CELL B							
high purity iron alloy B.C.S.No.260/2 0.009%	2g/ 100 ml from 100 g	0.0018mg 0.03051mM In 100 ml Draw 8ml	0.02441mM 0.01440 mg	0.02422Mm In 10 ml 0.03027 mM in 100 ml	0.17859mg 8.92965mg	0.00893%	99.23%
				0.02336 mM In 10 ml 0.02919 mM in 100 ml	0.17225mg 8.61255mg	0.00862%	95.70%
high purity iron alloy as granules B.C.S.No.149/2 0.012%	2g/ 100 ml from 100 g	0.024mg 0.04068mM In 100 ml Draw 8 ml	0.03254 mM 0.19199 mg	0.03096 mM In 10 ml 0.03870 mM in 100 ml	0.22833g 11.41669mg	0.0114	95.14%
				0.03599mM In 10 ml 0.04499mM in 100 ml	0.26543 13.2713mg	0.01327	110.59%

## Conclusion

A challenging well designed that has taken into account all possibility with the available electronic pieces that a new instrument come into a real manufacture and put into real use. The instrument presented here is only part of the potential uses of NAG-ADF-300-2. It shows the flexibility of using the instrument applied to precipitation reaction (in this part precipitation of Cobalt (II) ion with rubeanic

acid reagent in alkaline medium) Confidence of trusty measurable repeated for successive measurements shows an excellent reproducible and repeatable measurement. Stability of measurements is a crucial factor in trusting a new instrument. No low band electronic RC-filter was used to obtain good S/N. Extend ability of the calibration graph with the mathematical equation that support more than 99%of the results .Also digital

data smoothening of Savitzky - GOLAY was applied and it shows a good agreement of both mathematically fit equation and Savitzky-Golay treatment; which is a very well accepted digital filtering. The whole

process of measurements and data handling and its application shows that NAG-ADF-300-2 analyser is a new horizon in instrumental ON-LINE flow injection analysis; never tried or thought before.

## References

- Greenwood NN, Earnshaw A (1997) Chemistry of the elements, Butter Worth, 2<sup>nd</sup> Ed, London, 1117-1119.
- Enghag P (2004) Encyclopedia of the elements; Technical data-history-processing Applications, Wiley- VCH, New York, 667.
- Krebs, Robert E (2006) The history and use of our earths chemical elements: A reference guide, Greenwood Publishing group, 2<sup>nd</sup>ed, USA, 107.
- Petitto SC, Marsh EM, Carson GA, Langell A (2008) Cobalt oxide surface chemistry: The interaction of Co O, Co <sub>2</sub>O<sub>3</sub> and Co <sub>3</sub>O<sub>4</sub> with oxygen and water, journal of molecular catalysis A: Chemical, 281: 49-58.
- Reddy BR, Radhika P, Kumar JR, Priya DN, Rajgopal K (2004) Extractive spectrophotometric determination of cobalt (II) in synthetic and pharmaceutical samples using cyanex 923 , Analytical sciences, 20 (2): 345-349.
- Malik KN, Kaul KN, Lark BS, Faubel W, Rao ALJ (2001) Spectrophotometric determination of cobalt, nickel, palladium, copper, ruthenium and molybdenum using sodium isoamylxanthate in the presence of surfactants, Turkish journal of chemistry, 25 (1): 99-105.
- Shar GA, Soomro GA (2004) Spectrophotometric determination of cobalt (II), nickel(II), and copper (II) with 1-(2-pyridylazo) -2- naphthol in micellar medium , The nucleus, 41: 77-82.
- Veerachalee N, Taweema P, Songsasen A (2007) Complexation and spectrophotometric determination of cobalt (II) with 3-(2-thiazolylazo)-2, 6-diaminopyridine, Kasetsart journal natural science, 41(4): 675-680.
- Issam MA Shakir, Nagam S Turkey Al-Awadi (2013) Spectrophotometric-Continuous Flow Injection Analysis(S-CFIA) For The Determination of Cobalt(II) Ion in River & Alloy Samples Via The Use of 10,10-Dimethyl 9,9-Diacridinium Dinitrate Salt-Hydrogen Peroxide in Alkaline Medium , kərbala journal of Science, 11(3):244-258 .
- Garcia-Campana AM, Baeyens WRG (2001) Chemiluminescence in analytical chemistry, Marcel Dekker, Inc, New York, 1190.
- Turkie NS, Shakir IMA (2005) New mode for the study of chemiluminescence reaction by tracking via multi detection points through optical fibers in a completely newly designed cell, P.hD thesis, Baghdad university ,230
- Weisz H, Pautel S, Diger CM, Glatz U (1984) Application of fluorescence reactions in the ring over segment technique, Micro Chim Acta, 1(1-2): 69-82.
- Yousif NM, Shakir IMA (1993) On-line ultra trace determination of Co(II) ion and hydrogen peroxide through simulated insitu fluorescence using fluorophor molecule individually or through chain energy transfer process, M. Sc thesis, Salahaddin university, 125.
- Yamane, T, Watonabe K, Mattala HA (1988) Continuous flow system for determination of cobalt in sea and river water. In line pre-concentration separation coupled with catalytic determination, Yamanshi Univ, Japan, 207(1-2): 331-336, (Anal. Abs. 51(1989), 1H51).
- Helena RS, Marcela AS, Antonio OSR (2003) Using of mixing chamber for sample preparation and multiple collection in sequential injection analysis determination of sulphate in wines. J. Braz. Chem. Soc., 14(1): 59-64.
- Vogel A I (1953) Text- book of macro and semi micro qualitative inorganic analysis, 4<sup>th</sup> Ed, Longmans, green and Co. LED. William glows and sons, limited, London, 227: 282.
- Abraham Savitzky, Marcel JE Golay (1964) Smoothing and differentiation of data by simplified least square procedures, Anal. Chem., 36 (8): 1627-1639.
- Bluman AG (1998) Elementary Statistics, 3<sup>rd</sup> Ed, WCB/MC Graw-Hill, New York, 674
- Miller JC, Miller JN (2010) Statistics for analytical chemistry. 6<sup>th</sup> edition. John Wiley & N.Y Sons Pearson education limited, UK.
- Brink D (2010) Essentials of statistics. Ventus publishing ASP.