Journal homepage www.jzs.uos.edu.krd
Journal of Zankoi Sulaimani
Part-A- (Pure and Applied Sciences)

Spectrophotometric determination of Cobalt II with PAN using Flow injection technique

Sherwan O. Baban

Chemistry Department, College of Education Science, University of Salahaddin Erbil-Iraq

E-mail: Shirwan_baban@yahoo.co.uk

Article info

Original: 17 Apr. 2015
Revised: 25 May 2015
Accepted:30 August 2015
Published online:
20 Dec. 2015

Key Words:
Cobalt, PAN, Spectrophotometry, flow injection.

Abstract

A simple, rapid, reproducible and sensitive spectrophotometric method for determination of Cobalt (Co^{2+}) was investigated .The method was based on the interaction of Co^{2+} with 1-(2-pyridylazo)2-naphthol (PAN), in the presence of buffer pH 6 ($CH_3COOH + CH_3COONH_4$) to give a highly colored species of a molar ratio 1:2 (Co:PAN) .Beers law was obeyed in the range of (0.1-2.5) µg/ml with the molar absorptivity of $3.77x10^4$ $L.mol^{-}.cm^{-}$ at λ max 525 nm. The method was adapted to semi automated flow injection system .The molar absorptivity was $0.16x10^4$ $L.mol^{-}.cm^{-}$ at λ max 525 nm .Beers law was obeyed in the range (0.3-10) µg/ml. The precision and accuracy studied to both systems. The method was applied successfully to the assay of Co^{2+} in real sample such as real water and waste water, and was well agreed with its certified value.

1: Introduction

Cobalt is an important element for industry, due to its strength and high resistance to corrosion in many media, it is widely used in high-speed steel tools, magnets and high temperature alloys [(1)]. Its salts are useful in paint dryers as catalyst, abrasion resistance glasses, ceramics, and batteries and in production of numerous pigments like cobalt blue and cobalt green [(2)]. Cobalt is also used as a catalyst in industrial processes, pharmaceutical and biological systems [(3)]. Cobalt is component of vitamin B_{12} which has important role in many biological processes, such as erythrocyte formation, and its deficiency can lead to pernicious anemia. The recommended dietary allowance (RDA) for vitamin B_{12} for adults is 2.4 mg day^{-1} which contains 0.1 mg of Cobalt. However in larger amounts it is toxic and has been reported to produce pulmonary disorders, dermatitis, nausea, vomiting, diarrhea, blood pressure, slowed respiration, hyperglycemia and so on [(2)]. Cobalt at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Co can

bind to the cell membrane and hinder the transport process through the cell wall. Co at nearly 40ng mL^{-1} is required for normal metabolism of many living organisms [4].

Thus, due to the clear need for determining of Co^{2+} ions in many industrial, environmental medicinal and food samples, there are a lot of techniques being developed for Co sensing. There is an increasing demand to develop simple, sensitive, and selective analytical technique that do not use expensive, or complicated test.

In the determination of trace cobalt, various methods including inductively coupled plasma mass spectrometry (ICP-MS), spectrofluorometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), anodic stripping voltammetry, GFAAS [1], differential pulse cathodic voltammetry [5], LC Switching Column Method with UV/VIS detection [6], X-ray Fluorescence spectrometry , Atomic absorption spectrometry, and Chemiluminescence [7-13], have widely been used or applied. Among these techniques, GFAAS, ICP-MS, and anodic stripping voltammetry can be directly applied to the determination of Co^{2+} at the ng.mL^{-1} level. Among these, predominantly spectrophotometric methods are preferred, as they are less expensive and possess a greater sensitivity in comparison.

However, some of these methods are time-consuming and require complicated and expensive instruments and are not free from matrix effects [1].

A wide variety of spectrophotometric method for the determination of Co^{2+} have been used. The main chromogenic reagent are: Pyridylazo reagents, Thiazolylazo reagents, benzo thiazolylazo reagents, 8-aminoquinoquionoline proplyrins, nitroso dyes and the similars [14-17].

The possibility of using 1-(2-pyridylazo)-2-naphthol (PAN) for the analytical purposes was investigated by Cheng and Bray. This reagent reacts with many metal ions in the periodic table to form water-insoluble, coloured chelate complex and has been applied widely in the liquid extraction and spectrophotometric determination of metal ions in materials [18].

The structure of PAN is shown in Fig (1a). It contains a replaceable hydrogen atom, and a nitrogen atom suitably locate to form chelate rings. It is an orange amorphous solid, nearly insoluble in water, but soluble in alkali and a variety of organic solvents to which it imparts a yellow colour. The maximum absorbance of the reagent in organic solvents is at 470 nm. The reagent is very stable even in the presence of oxidizing agents. Also the reaction centres of the reagent are shown in Fig (1b) [19].

PAN is very stable in solid state and can be kept for many years in an amber bottle and is almost insoluble in water, slightly soluble in strong acid, in aqueous alkali, and in various organic solvents. The dye is noted for its high sensitivity, the stability of its complexes, and the characteristic colour change produced on chelation. The great advantage of PAN is that its solutions and also solutions of its complexes are usually stable for such a sensitive reagent [20].

However, its use in direct spectrophotometric analysis is restricted due to its non-selective and hydrophobic nature. In addition, most of the PAN–metal chelates exhibit similar absorption maxima in the region of 560–580 nm. Elimination of interferences would allow the precise and more selective determination of trace elements even at sub-microgram per liter levels by the same reagent [21].

In this investigation, the simple and rapid batch method was used for determination of Cobalt (II).

The main aim of the study was to convert a batch method to a semi-automated flow injection analysis system.

2: Experimental

Apparatus

UV –Visible spectrophotometer (4050 LKB Biochromulfra Spc II). LKB 2210 – 2 channel recorder. Philips ion selective meter (PW9415). Peristaltic pumps ((Waston-Maslow type 2024.Multi channel. Flow cell of two mm path length quartz. Six wax loupe valve with various sample lamps.

3: Reagents and chemicals

All reagents in this experimental were of analytical grade. Deionized distilled water (DDW) was used as a matrix for reagents, and standard solutions. Stock solution of Co^{2+} (1000 ppm), was prepared by dissolving 3.1017 g of $Co(NO_3)_2$ In 1 L of DDW. PAN solution ($4x10^{-4}$M) in ethanol. 0.1 g of PAN was dissolved in 1 L (Ethanol 95%, the solution was stable for one week only).

4: Procedure

4.1: for batch method

For batch preliminary method, the spectrophotometer was setup at 525 nm.

$4x10^{-4}$ M PAN, 10 ppm of Co^{2+}, and buffer (acetic acid + acetated) was used**.**

5 ml of buffer + 5ml of Co^{2+} + 5ml of PAN, were mixed, the final volume was 25 ml completed by deionized distilled water (DDW), and the absorbance was taken.

4.2: For Flow Injection method

For Flow Injection method, the spectrophotometer was setup at 525 nm also.

The carrier stream of the buffer solution adjusted to pH 6 was pumped through a flow rate 1.5 ml /min and the reagent at 0.5 ml/min .In this setup a known volume of sample (85µl) was injected directly through the

injection valve to a buffer solution line. The sample and buffer was mixed in 20 cm coil , and this stream was mixed with reagent line in 60 cm coil .An cobalt- PAN complex was formed which passed through a flow cell, and the peak height of the complex was observed as a signal graphically on a chart recorder. Fig 2 shows the schematic diagram of the flow injection system for the method.

5: Result and discussion

Spectrophotometric determination of Cobalt (II) with PAN, by batch and Flow injection methods.

5.1: Batch method

The absorbance change of the solution monitored at λ- max =525nm, conc. of standard solution of Co^{2+} = 10 ppm, conc. of PAN = 100 ppm

Buffers: from 1-7 pH CH_3COONH_4/CH_3COOH

Buffers: from 8-12 pH CH_3COONH_4/NH_4OH

5.1.1: Study of Buffer

5 ml buffer + 5ml Co^{2+} + 5ml PAN completed to 25 ml with DDW. The best pH was 6 as shown in table 1.

5.1.2: Study of Reagent

5ml buffer + 5ml Co^{2+} + x ml of PAN (1000ppm) completed to 25 ml with DDW. The best volume was 3 ml with final concentration of 12 ppm as shown in table 2.

5.1.3: Study of the buffer volume

x ml of buffer + 5ml Co^{2+} + 3 ml of PAN completed to 25 ml with DDW. The best volume was 4 ml as shown in table 3.

5.1.4: Study of the effect of time on the stability of complex formation of (Co-PAN)

4ml of buffer + 3ml of PAN (1000ppm) + 5ml Co^{2+} 10 ppm completed to 25ml with DDW. The best stability was after 30 min as shown in table 4.

5.1.5: Order of addition

In the same way of (D orders) of additions were held the results as shown in table 5, had no effect on the absorbance.

5.1.6: Nature of the complexes

The nature of the complexes were studied continuous variation methods as follows:

9 conical flask of 25 ml volume contain 1-9 ml of Co^{2+}, and 9-1 ml of PAN respectively, added to each flask 4 ml of buffer solution pH 6, and the results are shown the complex is ML_2 as shown in table 6.

5.1.7: Calibration curve

Linear equations from Calibration is y= 0.0632+0.3648x, r= 0.9999 as shown graphically in Fig 3.

5.1.8: Precision and accuracy

Table 7 shows the standard deviation (S.D), relative standard deviation (RSD), and %E of the batch method for determination of (0.1, 0.5 and 2) ppm of Co(II).

5.2: Flow injection method

5.2.1: Optimization

Table 8 shows physical and chemical optimizations for the method the results were summarized as optimum conditions in Table 9.

5.2.2: Calibration curve

Under the optimized condition as in Table 9, Fig3 shows the calibration graph between the concentration of Co(II) and peak height (mm).

The calibration curve is linear in (0.3-10) ppm with detection limit of 0.1ppm with the following least square regression equation:-[y=0.855+13.9x] with correlation coefficient of 0.9996.

5.2.3: Accuracy and precision

Table 10 shows the standard deviation (S.D), relative standard deviation (RSD), and %E of the FIA determination of (0.3, 1.0 and 5) ppm of CoII.

5.2.4: The sensitivity of the method

The molar absorptivity (ε) is ($0.16*10^4$) $l.mol^{-1}.cm^{-1}$ at λ_{max} 525 nm. The results show that the method is sensitive and accurate in the range of (0.3-10) ppm.

5.2.5: Effect of interferences

The effect of foreign ions on the determination of 5 ppm of CoII was studied.

Table 11 shows the maximum amounts of interfering ion that causes different errors between (0 - 2.86) %.

6: Applications

Table 12 shows the Co (II) found in a different real water .The results show that the method is quite suitable for determination of Co (II) in tap and waste water.

7: Conclusion

The proposed method gives a precise, sensitive, low cost and selective procedure for determination of cobalt (II) based on the color formation upon complexation between Co^{2+} ions and 1-(2-pyridylazo)2-naphthol (PAN) reagent. Although both of the detection limit and the sensitivity of the batch method are higher than the automated flow method, the later has its greater advantages like, reproducibility, reliability, saving of chemicals, saving of time, feasibility and high performance (100 s/h).

The method can be applied for determination of different types of samples.

a **b**

Figure1: (a) Structure of 1-(2-pyridylazo) 2-naphthol (PAN)

(b) Functional groups of PAN

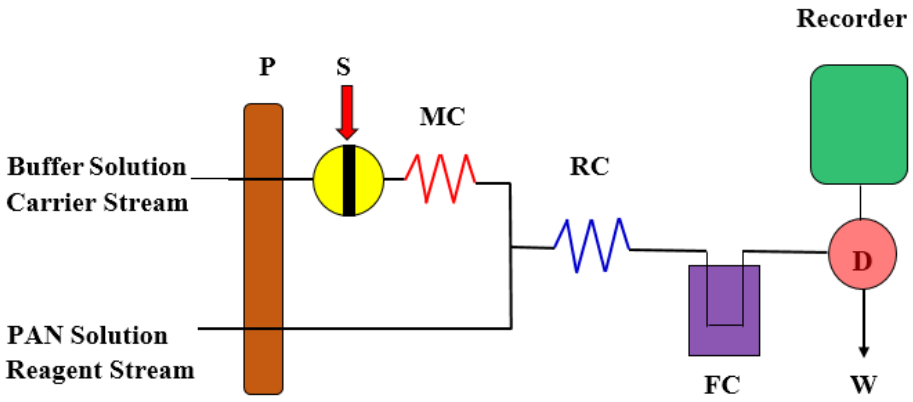

Figure2: Schematic diagram of FIA system used for determination of Co^{2+}

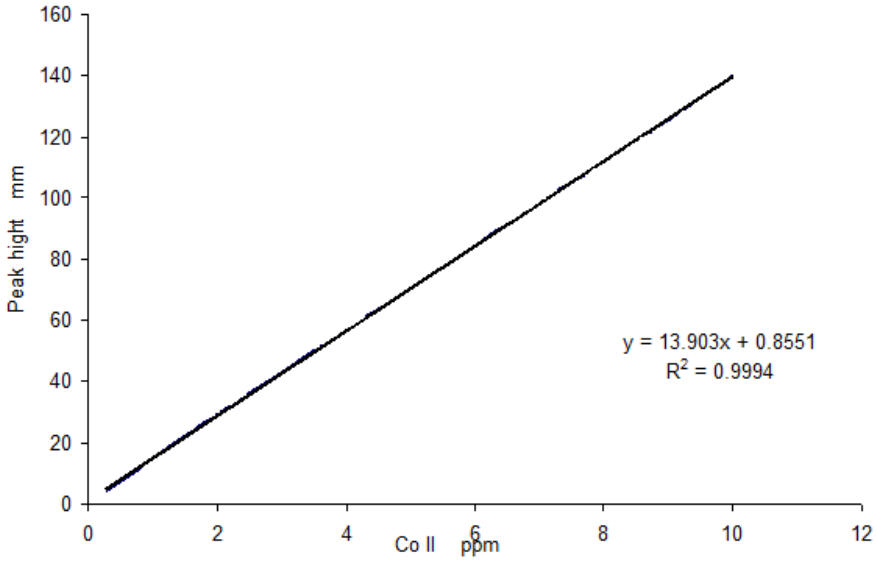

Figure3: Calibration curve of determination of Co (II) by using PAN reagent and FIA technique

Table 1: Effect of different type of buffers

pHs	1	2	3	4	5	**6**	7	8	9	10
Absorbance	0.132	0.367	0.558	0.595	0.630	**0.795**	0.79	0.79	0.72	0.708

Table 2: Study of the effect of reagent PAN in volume

Volume of PAN / ml	Absorbance	Final concentration of PAN ppm
1	0.280	4
2	0.520	8
3	**0.820**	**12**
4	0.795	16
5	0.793	20
6	0.600	24
7	0.600	28
8	0.550	32

Table 3 : Study of the buffer volume

Volume of Buffer	1	2	3	**4**	5	6	7
Absorbance	0.250	0.520	0.720	**0.840**	0.830	0.7	0.19

Table 4: Study of the effect of time on the stability of complex formation of (Co-PAN)

Time in minute	1	5	10	15	20	25	**30**
Absorbance	0.830	0.780	0.600	0.310	0.100	0.005	**0.005**

Table 5: Study of the order of addition

Orders of addition	Absorbance
B+M+R	0.850
M+ B+R	0.827
R+M+B	0.831
M+R+B	0.830
R+B+M	0.829
B+R+M	0.830

Table 6: Study of the nature of the complexes

Vm/Vm+Vl	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Absorbance	0.2	0.4	0.65	0.98	0.79	0.600	0.510	0.310	0.100

Table 7: Study of the precision and accuracy of the batch method for determination of CoII

Conc.	Abs.	Mean	S.D	R.S.D	%E
0.1	0.1 0.105 0.103	0.1026	$2.518x10^{-3}$	2.454	-2.534
0.5	0.245 0.241 0.243	0.243	$2.0x10^{-3}$	0.8230	+0.823
2	0.793 0.790 0.795	0.7926	$2.518x10^{-3}$	0.3176	+0.0504

Table 8: Physical and chemical optimization for spectrophotometric determination of CoII with PAN using flow injection technique.

Optimize Parameters	**Variables**		**Measurement**						
Physical	Reagent flow rate	ml/min	0.5	**1.0#**	1.5	2.0	2.5		
		p.h(mm)	20	**25**	23	17	10		
	Buffer flow	ml/min	0.5	0.75	1.0	**1.25#**	1.5	2.0	

	rate	p.h(mm)	15	17	23	**27**	25	20	
	Mixing coil length	cm	0.0	**20#**	30	40	50		
		p.h(mm)	20	**27**	23	20	15		
	Reaction coil length	cm	20	40	60	**80#**	100	120	
		p.h(mm)	17	2	27	**35**	35	30	
	Sample volume	µl	25	50	75	**85#**	100		
		p.h(mm)	25	28	30	**35**	36		
Chemical	pH effect	pH	3	4	5	**6#**	7	8	9
		p.h(mm)	0.0	15	25	**35**	33	30	20
	Reagent concentration	[PAN] $*10^{-3}$	0.5	0.75	1.0	**1.25#**	1.5		
		p.h(mm)	20	30	35	**40**	variable		

p.h=peak height

#=optimize number

Table 9: Optimum conditions used for CoII by PAN using FIA

Parameter	Value
λmax	525 nm
Flow rate of reagent	1.0 ml/min
Flow rate of buffer	1.25 ml/min
Length of mixing coil	20 cm
Length of reaction coil	80 cm
Sample	5ppm CoII
Sample volume	85µl
pH of buffer	6
[PAN]	$1.25*10^{-3}$

Table 10: Precision and accuracy of the method

Conc. Of CoII/ppm	Peak height (mm) mean (n=5)	S.D	RSD%	E%
0.3	4.1	0.5	1.6	+2.5
1.0	15	0.4	0.4	0.0
5.0	71	0.5	0.1	+1.4

Table 11: Effect of foreign ions on the determinations of 5 ppm of CoII.

Interfering ion added	Amount added	Error%
Al^{3+}	200	+0.7
Cr^{3+}	150	+1.43
Zn^{2+}	250	+2.14
Cd^{2+}	100	+2.86
Fe^{3+}	100	+0.7
Cu^{2+}	10	+2.86
Ni^{2+}	5	+2.14
NH_4^+	500	0.0
Cl^-	500	0.0
Br^-	500	0.0
CO_3^{2-}	500	0.0

Table 12: Determination of CoII in different real samples.

sample	CoII spiked mg/l	Found mg/l
Tap water (Erbil city)	1	1+0.1
Tap water (Erbil city)	5	5+0.01
Waste water(Erbil city)	5	5+0.1

Reference

1. A. Kaur, U. Gupta, S. S. Saini and A.L.J. Rao," Spectrophotometric determination of Co (II) in various samples by Solid phase Extraction using Chemically Modified SiO2-PAN Nanoparticles", Journal of Applicable Chemistry, 2012, 1 (3), pp. 381-391.
2. A. Beiraghi, M. Roshdi, "Development and characterization of a new cobalt optical sensor based on incorporating of salophen in a PVC matrix", Vol. 2, Issue 3, 2011, pp. 4-9.
3. W. Zhehui, J. Zhiruo, D. Xuechang, M. Mingming and Hu. Qiufen, "http:// www.chemistry mag.org // cji/2004", 6(2004)51.
4. A. Moghimi, "Preconcentration trace amount Co (II) by carbon nanotubes in water samples and determination it by FAAS", Journal of Applied Chemistry, 2014, 2(2), pp. (55-64).
5. M. R. Khan and S. B. Khoo, "1-(2-Pyridylazo)-2-naphthol modified carbon paste electrode for trace cobalt (II) determination by differential pulse cathodic voltammetry", the Analyst journal, Vol. 123, June 1998, pp. (1351–1357).
6. L. Tzanis, P. Simon, A. Walcarius, "Simultaneous Determination of Nickel and Cobalt as Chelates with 1-(2-Pyridylazo)-2-naphthol Using an LC Switching Column Method", Chromatographia , vol.67, No. 11/12, June 2008, pp. (857-861).
7. J. Pauwels, C. Hofmann, H. Grobecker and K. Fresemius, J.Anal.Chem. , " Micro-heterogeneity of trace elements in reference materials — determination and statistical evaluation", 345(1993)475.
8. AI. Yuzefovsky, RF. Lonardo and RG. Michel, Anal.Chem. , 67(1995)475.
9. A. Chow, GF. Yamashita and RF. Hamon, "Spectrophotometric Determination of Cobalt (II) Using 4-(6-Nitro-2-benzothiazolyl azo) resorcinol", Talanta, 28(1981)437.
10. QE. Cao, and SQ. Wu, "Study on the mechanism and applications of the fluorescence reactions among cobalt (II), H2O2 and two new derivatives of 8-sulfonamidoquinoline", Talanta, 51(2000)615.
11. B. Maziere, J. Gros and DJ.Comar, J.Radioanal.Chem. , 24(1975)207.
12. W. Ma, M. Guo, Chinese Journal of ph and ch. Analysis, 35(1999)284.
13. S. Li, L. Wang and C. Zhou, Chinese journal of Metallurgical Analysis, 20(2000)34.
14. H. Watanabe, "Spectrophotometric determination of cobalt with 1-(2-pyridylazo)-2-naphthol and surfactants", 21(1974)295.
15. LM. Siroki, L. Maric and Z. Stefanac, "characterization of complexes involved in the spectrophotometric determination of cobalt with 4-(2-pyridylazo) resorcinol". Anal. Chim. Acta, 75(1975)101.
16. MR. Khan, and SB. Khoo, "Spectrophotometric Determination of Cobalt (II) Using 4-(6- Nitro-2-benzothiazolylazo) resorcinol", Analyst, 123(1998)1351.
17. HB. Singh, NK. Agnihotri, and VK. Shigh, "Non-extractive derivative spectrophotometric determination of cobalt in neutral micellar medium", Talanta, 48(1999)623.
18. F. S. MAHANI and M. A. TAHER, "Application of 1-(2-Pyridylazo)-2-naphthol for Separation and Preconcentration of Trace Amounts of Cobalt (II) in Various Samples and Its Determination by Flame Atomic Absorption Spectrometry", Asian Journal of Chemistry Vol. 19, No. 4, (2007), pp. (2541-2549).
19. S. O. Baban, 1982, Ph.D. Thesis, "Development in flow injection analysis", 15- 17, 60.

20. Z. Safari, M.B. Gholivand, L. Hosseinzadeh, "Spectrophotometric study of complex formations between 1-(2-pyridylazo)-2-naphthol (PAN) and some metal ions in organic solvents and the determination of thermodynamic parameters", Spectrochimica Acta Part A, vol. 78, (2011), pp. (1606–1610).
21. E. K. Paleologos, M. I. Prodromidis, D. L. Giokas, A. Ch. Pappas, M. I. Karayannis, " Highly selective spectrophotometric determination of trace cobalt and development of a reagentless fiber-optic sensor", Analytica Chimica Acta, 467 (2002), pp. (205–215).