Flow-injection spectrophotometric determination of cadmium with PAN in DMF media

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Abstract

Determination of $Cd^{2+}$by spectrophotometric method with flow injection analysis was studied using PAN as a reagent in DMF media . Cd^{2+} was determined spectrophotometrically in pH 9 (The buffer produced from NH_4OH,CH_3COONH_4) and λmax 550nm using PAN as a reagent in DMF, Beer-Lambert low was obeyed in the range (0.05-2 mg/l) with detection limit was 0.04 mg/l , $\varepsilon=5.4*10^4$L/mol.cm .Precision and accuracy of the method were studied (S.D=$1*10^{-3}$,%E=-0.18-+2.56) and interferences of dominant cations were studied . The method converted to flow injection analysis in pH 8.5 the range became (0.5-8 mg/l) in the same λmax , solvent and reagent ,detection limit become 0.2 mg/l, $\varepsilon=1.2*10^4$L/mol.cm . Precision and accuracy of the method was studied (S.D=0.28_-3.6,%E=-2.17-+1.72) and interferences of dominant cations were studied . 90 sample was determined in one hour in FIA. This method could be applied to the rapid and simple determination of cadmium in real sample .

Introduction:-

The cadmium metal is very important , its very wide used (about three-fourth of cadmium is used in batteries – especially Ni-Cd batteries -)[1].Thin film of cadmium may be applied by electro-plating (or ,less importantly, by vaccum deposition , dipping or spraying) to ferrous metal surfaces to retard corrosion [2]. The rather high cost may thus be worth while in special applications. Because of its great neutron-absorbing capacity, cadmium (especially the isotope ^{113}Cd) is used in control rods and shielding for nuclear reactors[3].Various methods used for determination of cadmium, including ICP-MS[4], ion chromatography [5], anodic stripping analysis [6], electro thermal atomic absorption spectrometry[7] and spectrophotometry[8-12]. Many of these methods are time consuming or require complicated and expensive instruments or the determination occurs in a solvent some times the complex will be precipitated in high concentration level

. In our study , the determination of cadmium was spectrophotometrically performed in DMF media .

Experimental:-

Apparatus:-

-Flow injection system:-

Fig.1 shows a schematic diagram of FIA system used for spectrophotometric determination of Cd^{2+}.

a. Peristaltic pump (Watson-Marlow type 202 U, multi-channel) was used to propel the buffer and reagent solutions.

b. Injection valve is a 6-way loop valve with various sample loops, used to inject the sample into the buffers carrier stream.

c. Detector, LKB Bio chrom Ultrospec II 4050 UV-Visible sprctrophotometer with a flow cell of 10mm oath length made of quartz .

r. Recorder, LKB 2210 2-channel .

- **A** Philips ion-selective meter PW 9415 used for pH measurements.

Same spectrophotometer used for batch method with quartz flow cell.

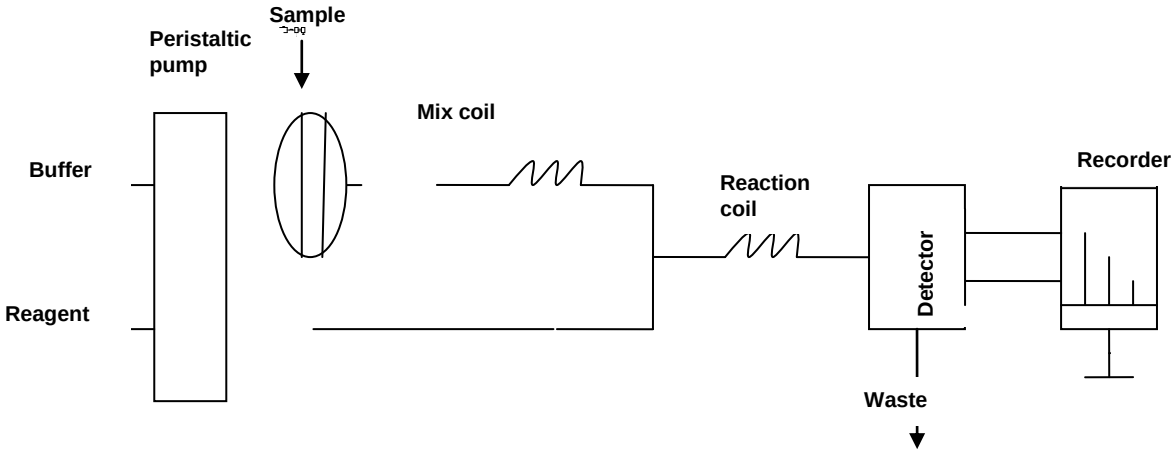

Fig.1:- Schematic diagram of spectrophotometric determination of $Cd^{2+}$by flow injection system.

-Reagents:-

All chemicals used were of analytical grade.

-Stock solution of Cd^{2+} (1000 mg/l) was prepared by dissolving 2.1032 gm of $Cd(NO_3)_2$ in 1L of distilled water.Tha dilute solution prepared from the stock solution.

-Preparation of PAN [1-(2-pyridyl azo)-2-naphthol] solution $4*10^{-3}$mol/l.

1 gm of PAN dissolved in DMF and the volume completed to1L with the same solvent.

A-Batch method:-

-Recommended procedure:-

The spectrophotometer was set at 550 nm .2ml of buffer solution [which produced from CH_3COOH + CH_3COONH_4 for acidic medium and NH_4OH + CH_3COONH_4 for basic medium] mixed with 2ml of Cd^{2+} solution (10 mg/l) this solution mixed with 2ml of PAN solution ($4*10^{-4}$mol/l) the solution completed to 25 ml with DMF and the absorbanse was read for a complex Cd-PAN by a detector which was used in FIA system.

-Result and discussion:-

-Optimization:-

Table 1 shows the optimum conditions for the determination of Cd^{2+} by batch method.The optimum conditions summarized in Table 2 which show that we can determine high level concentration of Cd^{2+}, 2mg/l.

Table 1 :- Optimum conditions for spectrophotometric determination of $Cd^{2+}$with PAN in DMF media*.

Variable		Measurements									
pH of buffer	pH	2 to5	5.5	6	6.5	7	7.5	8	8.5	9	9.5
	A	0.000	0.010	0.015	0.030	0.035	0.150	0.300	0.331	*0.331***	0.331
Volume of PAN ($4*10^{-4}$mol/l)	V_{PAN}/ml	1	2	2.5	3	4	5	6			
	A	0.026	*0.330*	0.333	0.332	0.330	0.332	0.332			
Volume of buffer	V_{buffer}/ml	1	2	3	4	5					
	A	0.16	0.33	*0.39*	0.34	0.3					
Time	Time/min	0	5	10	15	30	60	120			
	A	0.39	*0.39*	0.38	0.39	0.39	0.39	0.30			

***The order of addition don't effect on the absorbance.**

**** Best value.**

Table 2:- Optimum conditions for spectrophotometric determination of Cd^{2+} with PAN in DMF media by batch method.

Parameter	Value
pH	9
Volume of PAN ($4*10^{-4}$mol/l)	2 ml
Volume of buffer (CH_3COONH_4+NH_4OH)	3 ml
Stability of complex	About one hour
Molar of absorptivity	$5.4*10^4$ $l.mol^{-}.cm^{-}$

-The nature of the complex :-

The Cd^{2+}-PAN ratio is established by Jobs method of continuous variation . Fig.2 shows that the molar ratio of Cd^{2+} to PAN is found to be 1:2

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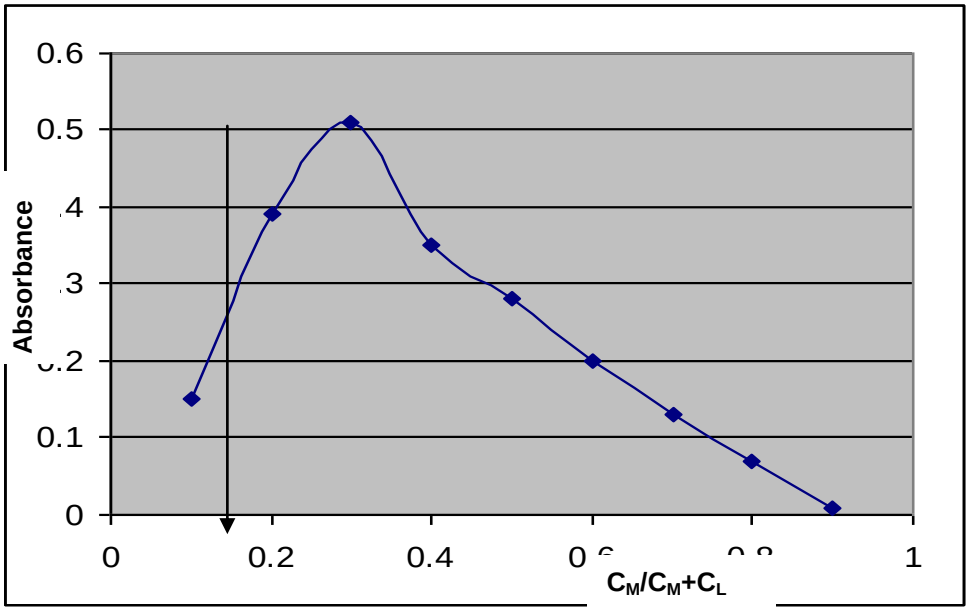

Fig2:-The nature of the complex Cd_PAN.

-Calibration curve:-

Under the optimized conditions as in Table2, the calibration graph between concentration of Cd^{2+} (mg/l) against the absorbance of complex is linear in wide range (0.05-2)mg/l of Cd^{2+} with the following least square regression equation :-$A=5.4*10^{-3}+0.48X$

With correlation coefficient of 0.9999,the detection limit is 0.04mg/l, as shown in Fig3.

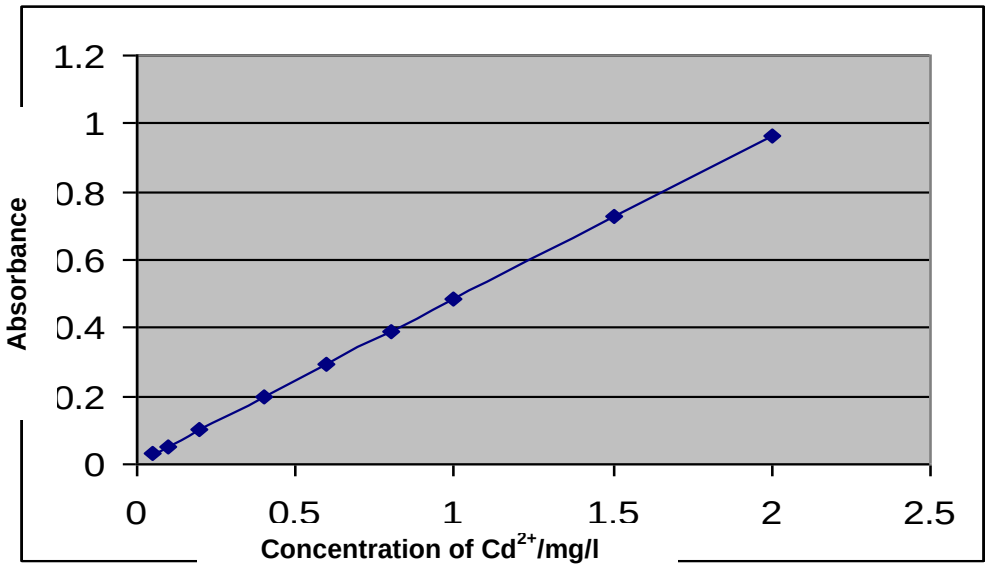

Fig.3:-Calibration curve for the determination of $Cd^{2+}$by batch method .

-Precision and accuracy:-

Table 3 shows the standard deviation S.D, relative standard deviation RSD and %E of the spectrophotometric determination of (0.1, 0.8 and 1.5) ppm of Cd^{2+}under the same optimum conditions. The results show that the method is reproducible, because the RSDis less than 2.5%.

Table 3 :- The precision and accuracy of the batch method.

Conc./ppm	A	S.D	RSD%	%E
0.1	**0.052 0.050 0.050**	**$1.155*10^{-3}$**	**2.280**	**+2.56**
0.8	**0.390 0.392 0.392**	**$1.155*10^{-3}$**	**0.295**	**-0.18**
1.5	**0.726 0.724 0.724**	**$1.155*10^{-3}$**	**0.159**	**-0.18**

-Selectivity of the method:-

The effect of five important cations was examined on the determination of 0.8 mg/l of Cd^{2+} which illustrated in Table 4, the studying show that the method is not selective method ,thus we try to determine Cd^{2+} by flow injection method

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Table 4 :- Effect of some interfering ions on the determination of $Cd^{2+}$by batch method.

Cations	Conc./ppm	A	%E
Co^{2+}	1	0.400	+2.56
Pb^{2+}	10	0.391	+0.256
Al^{3+}	10	0.389	-0.256
Zn^{2+}	1	0.398	+2.05
Cu^{2+}	1	0.396	+1.54

B-Flow Injection Method:-

-Recommended procedure:-

The spectrophotometer of the FI system was set at 550 nm. The carrier stream of buffer solution (adjusted at pH 9) was pumped through a flow rate 1.5 ml/min and reagent ($4*10^{-4}$ M of PAN in DMF) was pumped through a flow rate 1.5 ml/min too. The sample (2 ppm of Cd^{2+}) of the 100 µl was injected by the injection valve. The

sample and buffer were mixed in 20cm coil, and this stream was mixed with reagent (PAN)in 60cm coil. A Cd-PAN complex was formed which passed through a flow cell, and then peak height of the complex was obtained graphically at the chart recorder.

-Result and discussion:-

-Optimization:-

Table 5 shows physical and chemical optimization for the flow injection method , the method summarized as optimum conditions in Table 6 . Several types of buffer and organic solvents are studied , the results show that the best buffer is ($NH_4OH+CH_3COONH_4$ in pH8.5) and the best solvent is DMF.

Table 5 :- Physical and chemical optimization for Spectrophotometric determination of Cd^{2+} with PAN in DMF media by flow injection method.

Optimize parameters	Variables		Measurements								
Physical	Reagent flow rate	ml/min	0.5	0.75	1	1.25	1.5	1.72	2		
		p.h*/mm	15	18	22**	20	20	15	10		
	Buffer flow rate	ml/min	0.5	0.75	1	1.25	1.5	1.75	2		
		p.h/mm	15	20	27	25	22	20	15		
	Mix coil length	Length/cm	0	10	20	30	40	50			
		p.h/mm	12	18	27	25	20	10			
	Reaction coil length	Length/cm	20	40	50	60	80	100	120		
		p.h/mm	10	15	20	27	30	35	30		
	Sample volume	Volume/µl	25	50	75	85	100				
		p.h/mm	15	20	28	30	35				
Chemical	Buffer solution	pH	3-7	7.5	8	8.5	9	9.5	10	10.5	11
		p.h/mm	5	20	28	37	35	35	30	25	15
	[PAN]	[PAN]/M*10^{-3}	0.1	0.4	0.8	1	1.5	2	2.5		
		p.h/mm	30	38	45	47	49	50	Not stable		

*p.h=Peak height.

**Best number.

Table 6 :- Optimum conditions for Spectrophotometric determination of Cd^{2+} with PAN in DMF media by flow injection method.

Parameter	Value
Λmax	550nm
Sample	2 ppm Cd^{2+}
[PAN]	$0.8*10^{-3}$M
Flow rate of reagent	1 ml/min
Flow rate of buffer	1 ml/min
Length of mix coil	20 cm
Length of reaction coil	100 cm
Sample volume	100 µl
pH	8.5
Buffer type	$NH_4OH+CH_3COONH_4$

-Calibration curve:-

According the optimized conditions as in Table6 the calibration graph concentration of Cd^{2+} (mg/l) against the peak height in mm is linear in the range (0.5-8)mg/l of Cd^{2+} with the following least square regression equation A=0.998+22X

And the correlation coefficient is 0.9999,as shown in Fig.4 the detection limit is 0.2 mg/l Cd^{2+}.

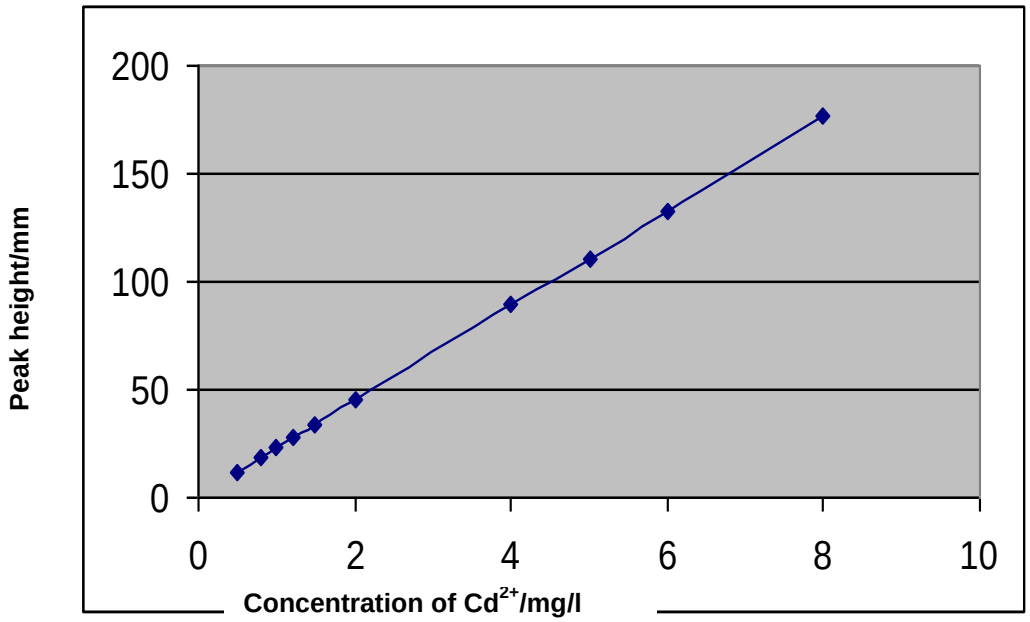

Fig.4:-Calibration curve for the determination of $Cd^{2+}$by flow injection method

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Precision and accuracy:-

Table 7 shows the standard deviation S.D, relative standard deviation R.S.D and %E of the flow injection spectrophotometric determination of (0.8,2 and 8) mg/l of Cd^{2+} under the same optimum conditions SD=(0.28-3.6), RSD=(1.5-2.1, %E= (-2.17_+1.72).The result show that this system is suitable for determination of Cd^{2+} in real sample.

Table 7 :- The precision and accuracy of the flow injection method.

Conc. of Cd^{2+} ppm	p.h/mm	S.D	RSD%	%E
0.8	18.5 18 18.5	0.2886	1.574	+0.90
2	45 46 47	1	2.174	-2.17
8	177 175 170	3.605	2.072	+1.72

-Effect of interferences :-

The interfering effect of various cations on the determination of 2 mg / l of Cd^{2+} were investigated under the optimum conditions given in Table6 are shown in Table8

Table 8 :- Effect of some interfering ions on the determination of 2ppm of $Cd^{2+}$by flow injection method .

Cations	Conc./ppm	p.h/mm	%E
Co^{2+}	10	47	+4.44
Pb^{2+}	50	46	+2.22
Al^{3+}	50	45	0.00
Zn^{2+}	10	47	+4.44
Cu^{2+}	10	47	+4.44

-Applications to real samples:-

After a given amount of Cd^{2+} was spiked in the solution containing some cations and anions ,recovery factor were determined using the calibration curve (to flow injection method) were found to be 101.31%. They are listed in Table 9. By these results we have concluded that this method could be applied to the determination of Cd^{2+}in real samples.

Table 9 :- Determination of Cd^{2+} by flow injection method in real samples.

Amount of Cd^{2+} added/ppm	Foreign ion	Amount of foreign ion/ppm	Measured Cd^{2+}/ppm(n=5)	%Recovery
0.8	Co^{2+},Zn^{2+},Cu^{2+} Pb^{2+},Al^{3+} NO_3^-,Cl^-,F^-	0.1 1 10	0.818	102.30
2	Co^{2+},Zn^{2+},Cu^{2+} Pb^{2+},Al^{3+} NO_3^-,Cl^-,F^-	2 5 20	2.091	102.91
8	Co^{2+},Zn^{2+},Cu^{2+} Pb^{2+},Al^{3+} NO_3^-,Cl^-,F^-	5 10 50	7.909	98.86

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الملخص

تم وصف طريقتين تقليدية وحقن جرياني طيفي لتقدير الكادميوم الثنائي في المحاليل المائية والنماذج الحقيقية ، أعتمدنا على مفاعلة الكادميوم الثنائي مع الكاشف بان (PAN) في المحلول المنظم (المتكون من الامونيا والخلات الامونيوم)ذي دالة حامضية ٩ في الطريقة التقليدية و ٨,٥ في طريقة الحقن الجرياني في وسط DMF . تم قياس الناتج الملون عند ٥٥٠ نانو ميتر . تمكنا من تطبيق قانون بير –لامبرت ضمن مديات التراكيز ٠,٠٥ – ٢ و ٠,٥ – ٨ مايكروغرام /مللتر لتقدير الكادميوم الثنائي و بحدود كشف ٠,٠٤ و ٠,٢ مايكروغرام /مللتر وامتصاصية مولارية ٥,٤*١٠ ^{٤} و ١,٢*١٠ ^{٤} لتر/مول.سم لكل من الطريقتين التقليدية و الحقن الجرياني على التوالي ز تم دراسة العوامل الفيزياوية والكيمياوية التي تؤثر على الطريقتين ، وطبقت الطريقة الحقن الجرياني بنجاح على تقدير الكادميوم الثنائي في بعض النماذج الحقيقية بدقة وتوافق جيدين .