

## A Simple Spectrophotometric Method for the Determination of Cadmium (II) using 1-(2-pyridylazo)-2-naphthol in Micellar Aqueous Solution of CTAB

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### Abstract

A simple rapid new spectrophotometric method has been developed for the determination of cadmium at trace level using 1-(2-pyridylazo)-2-naphthol (PAN) in cationic micellar solution of cetyltrimethyl ammonium bromide (CTAB). The present method with the use of micellar system replaces the previous solvent extraction method, which reduces the cost and toxicity, while enhancing the sensitivity, selectivity and the molar absorptivity. The average molar absorption coefficient and Sandell's sensitivity was found  $1.59 \times 10^4$   $\text{Lmol}^{-1}\text{cm}^{-1}$  and  $7.0 \text{ ng cm}^{-2}$  at  $\lambda_{\text{max}}$  544.86 nm. Beer's law linear calibration graph was obtained over the concentration range  $0.12\text{-}4.0 \mu\text{g mL}^{-1}$ , the stoichiometric composition of the chelate was 1:2 (Cd: PAN). The method was applied for the determination of cadmium from real samples.

*Key words:* Spectrophotometric, Cadmium, PAN, Micellar, Cationic, CTAB.

### 1. Introduction

The determination of trace and toxic concentration range of metal ions in biological life has become an interested field of modern scientific study. Cadmium constitutes the highest

environmental hazard due to their extensive use, toxicity and widespread distribution. Cadmium is non-degradable and so it accumulates in the environment<sup>1</sup>. The cadmium 10% is inhaled by the smokers from the total amount present in the tobacco<sup>2</sup>. Cadmium excess

accumulation causes hypertension in human body. Cd in higher concentration was found in the urine and kidneys of the hypertensive patients. The analysis of cadmium has received importance in the study of environmental pollution. In spectrophotometric analysis of metal ions, the metal is complexed with chelating agent and solubilized in solvent extraction is easy method for studying the metal ions because of its simplicity and rapidity<sup>3-6</sup>. Several spectrophotometric methods have been developed to replace the old solvent extraction method by using the surfactants<sup>7-12</sup>. Micellar media is introduced to enhance the molar absorptivities, sensitivities and replaces the previous steps of toxic solvent extraction<sup>13-19</sup>. We have developed a new simple, sensitive and selective spectrophotometric method for the determination of cadmium (II) in various materials by using PAN as chromogenic agent in cationic micellar solution of CTAB.

## 2. Experimental

### 2.1 Apparatus :

A UV-Vis scanning spectrophotometer (Cecil CE 9500 model) equipped with a 10-mm path length quartz cell was used. Atomic absorption spectrophotometer (Analyst-100 Perkin Elmer) with multi-elemental hollow cathode lamps was utilized. pH/ conductivity meter (Sension 156 HACH) with Sension Gel-filled pH electrodes was utilized. FTIR (Spectrum-One Perkin Elmer) was used.

### 2.2. Preparation of Reagents :

PAN (Merck) solutions of  $8 \times 10^{-3}$  M were made in 100 mL by dissolving its 0.1994 g in small volume of ethanol and diluted with

0.02 M CTAB surfactant solution. Cd(II) ions stock solutions of ( $1000 \mu\text{g mL}^{-1}$ ) were made and were standardized<sup>20</sup>. CTAB 0.02 M surfactant solution was prepared by dissolving its 0.02 g in 1000 mL. Sodium tartrate tetrahydrate salt 0.1% w/v and 2.0% (m/v) hydroxylammonium chloride solution was prepared. However, 30%  $\text{NH}_3$  concentrated solution 10 mL volume was diluted in 100 mL volumetric flask. Whereas, 0.1% w/v EDTA solution was prepared. Moreover, ( $1000 \mu\text{g L}^{-1}$ ) stock solutions of thiosulphate, ascorbic acid, sodium acetate, sodium thiosulphate and ammonium molybdate were made. Metal ions solutions ( $1000 \mu\text{g L}^{-1}$ ) were prepared by dissolving their appropriate salts and acidified<sup>21</sup>. Buffer solutions of pH 1-10 were prepared by using appropriate methods<sup>22</sup> with appropriate volumes of the mixtures of 0.2 M KCl - 0.2 M HCl for (pH 1-4.0), 0.2 M  $\text{CH}_3\text{COOH}$  - 0.2 M  $\text{CH}_3\text{COONa}$  for (pH 5-6.0), 0.1 M  $\text{KH}_2\text{PO}_4$  - 0.1 M NaOH for (pH 6.5-8.0) and 0.025 M sodium borate and 0.1 M HCl for (pH 9-10.0).

### 2.3 Preparation of sample solutions :

#### 2.3.1 Determination of cadmium ions in industrial waste water samples :

Waste water sample 1 L was collected from the area of industrial zone Sukkur city. The sample solution was filtered with Whatman filter paper then the sample was further dissolved and acidified with 30% hydrogen peroxide (2.0 mL) solutions and concentrated nitric acid (4.0 mL) solutions. The sample solutions obtained were further pre-concentrated in oven at  $110^\circ\text{C}$  to reach the final volume 25 mL solution. The sample was taken in calibrated flask, added appropriate volumes of 1 to  $5 \times 10^{-4}$  M

PAN, 0.02M CTAB (1mL) and buffers were added for the complex formation. The absorbance of metal chelate was recorded taking reagent blank as a reference for the metal ions determination in present technique. The data values are given in Table 6.1.4.

### 2.3.2 Determination of cadmium (II) ions in stream water sample :

The stream water solution was collected from Khairpur, Sindh city. The sample solution was filtered with filter paper and acidified with dil.  $\text{HNO}_3$ <sup>23</sup>. The 5 mL sample was transferred to three different volumetric flasks of 10 mL, and then added the optimized concentration of PAN, appropriate buffers and 0.02M CTAB for complex to the determination of Cu(II) ions by present method as given in Table 3-7.

### 2.3.4 Procedure for determination of cadmium (II) ions :

Cadmium 1.0 mol sample solution, 2.0 mL buffer solution of pH 9, (1mL) 0.02M CTAB solution and 1.0 mL  $5 \times 10^{-4}\text{M}$  PAN solutions were added to 10.0 mL volumetric flask and solution was investigated. Results were compared with AAS as given in the Table 3-7.

## 3. Results and Discussion

Cadmium (II) reacts with PAN forms [Cd(II)-PAN] complex as shown in Fig. 1. UV-Vis spectrum of PAN gives greenish colour of ligand-to ligand charge transfer (LLCT) ( $\pi \rightarrow \pi^*$ )<sup>24</sup> nitrogen atom of azo molecule at  $\lambda_{\text{max}}$  471 nm and <sup>25</sup> at UV 250 nm for oxygen of C-O-H as shown in Fig. 2. UV-

Vis spectrum of cadmium (II)-PAN complex red colour solution showed bathochromic shift of 88 nm charge transfer from ligand-to metal (LMCT) ( $p\pi-d\pi$ ) at  $\lambda_{\text{max}}$  544.86 nm as shown in Fig. 3. The stoichiometry of the complex was found 1:2 (Metal: Ligand). 1 m. mole Cd(II) ions and PAN molar ratio 1:  $4 \times 10^{-4}\text{M}$  was optimized for complex formation as shown in Fig. 4. The 0.02M CTAB 1mL showed maximum constant absorbance in  $2 \text{ mgL}^{-1}$  Cd(II)-chelate, that concentration is greater than cmc value  $(1.3\text{Mm})$ <sup>26</sup>. Cd-PAN complex showed maximum constant absorbance at pH 9.0 as shown in Fig. 5. Molar absorptivity of the complex was found  $1.59 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Calibration graph showed linear concentration range over the of  $0.12\text{--}4.0 \mu\text{g mL}^{-1}$ , the correlation coefficient with experimental data was 0.999 as shown in Fig. 6. Detection limit and Sandell's sensitivity was found  $0.12 \mu\text{g mL}^{-1}$  and  $7.0 \text{ ng cm}^{-2}$  as given in Table. 1. The metal-complex showed absorbance maximum constant up to 5 minutes. At ordinary temperature Cd-PAN complex showed stable absorbance measurement, till 24 h. Cd(II)-PAN complex in micellar solution was stable than solvent extraction system<sup>27</sup>. The developed method was validated to the determination of cadmium ions in real matrixes to verify the accuracy and the precision of the method. The average Cd ions found (n 7) in the reference material with a precision as relative standard deviation RSD was up to 0.91 %.

### 3.1 Effect of foreign ions in the determination of nickel :

The cations Cr(IV) and Co(II), showed much interference in the determination of

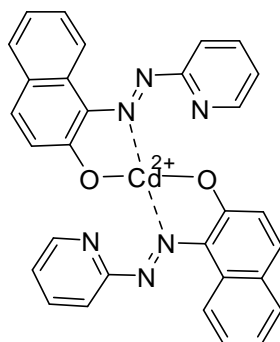
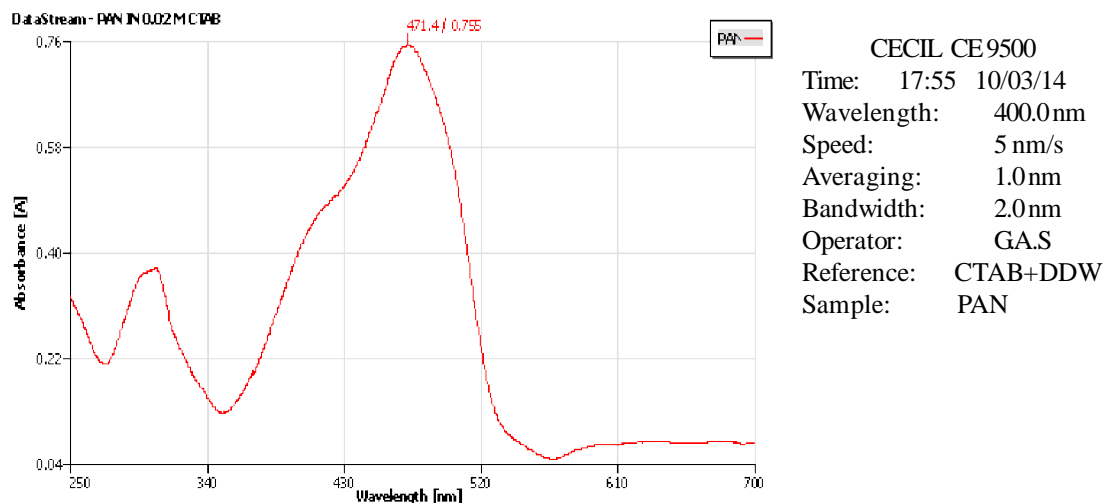
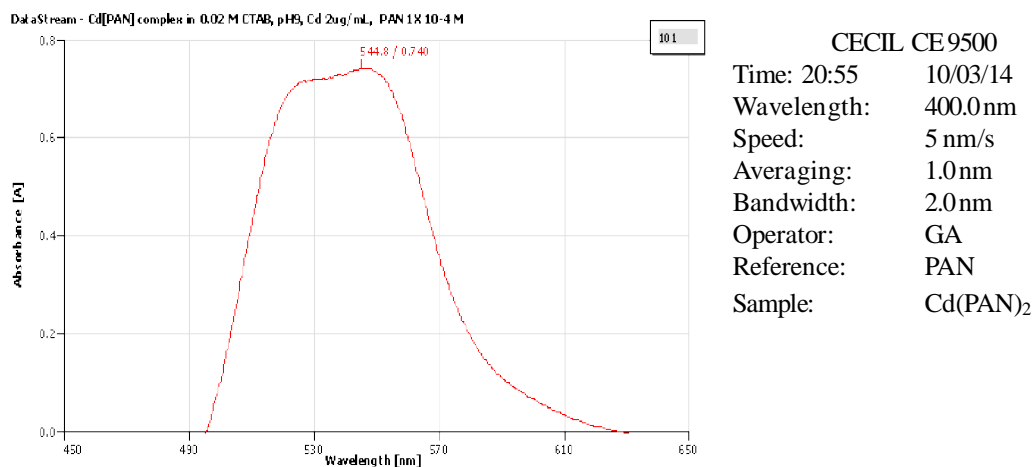


Fig. 1. Proposed structure for Cd(II)-PAN complex

Fig. 2. UV-vis spectrum of PAN at ( $\lambda_{\max}$  471.4 nm) neutral pH in 0.02 M CTABFig. 3. UV-vis spectrum of Cd(II)-(PAN) complex at ( $\lambda_{\max}$  544.86 nm) pH 9 in 0.02 M CTAB

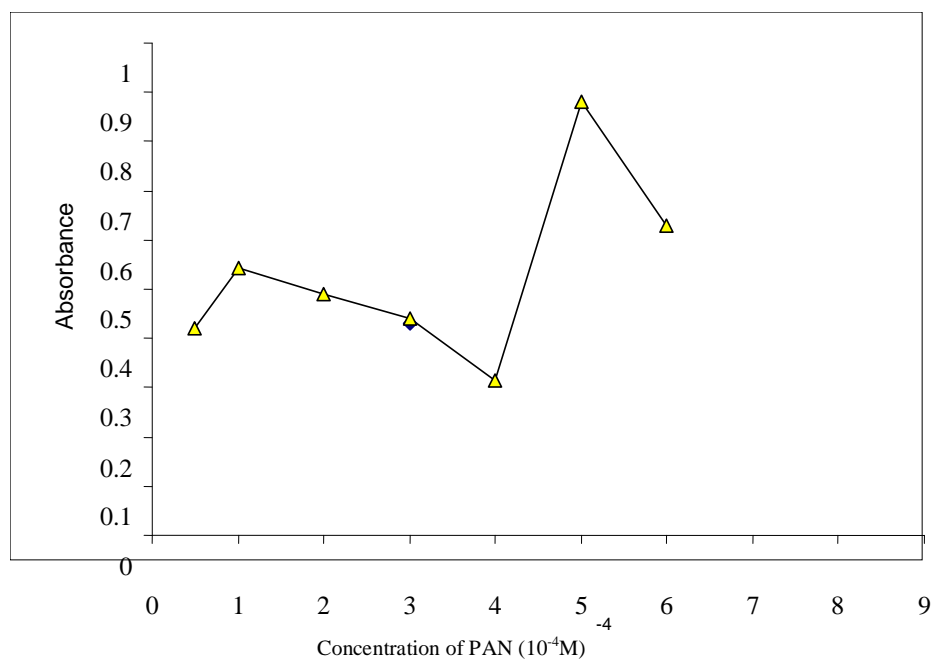
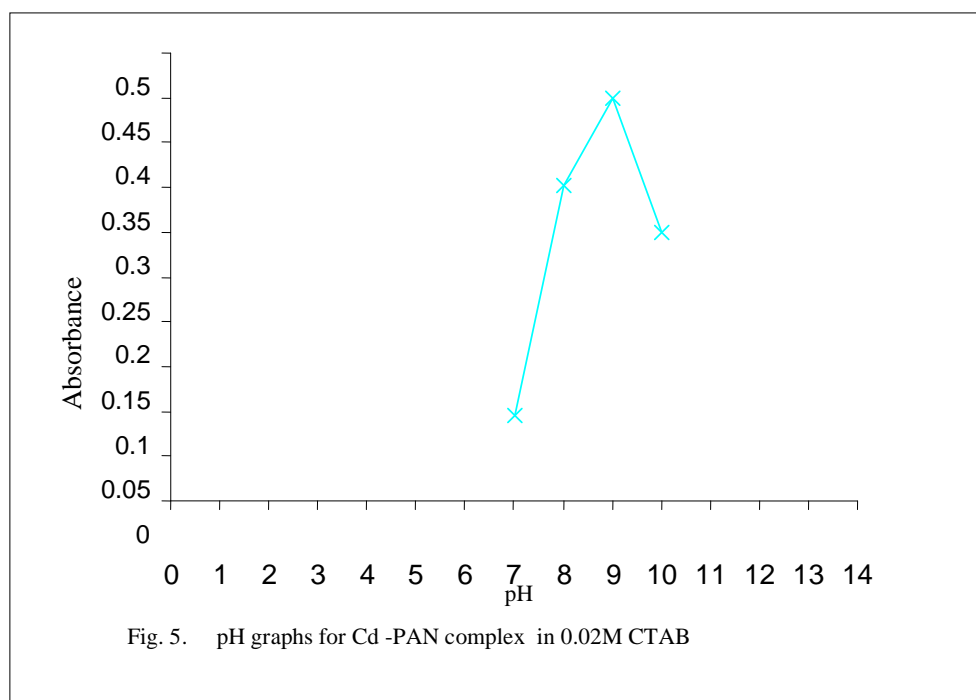


Fig. 4. PAN reagent of molar ratio concentration effect on the absorbance of Cd-PAN in 0.02M CTAB



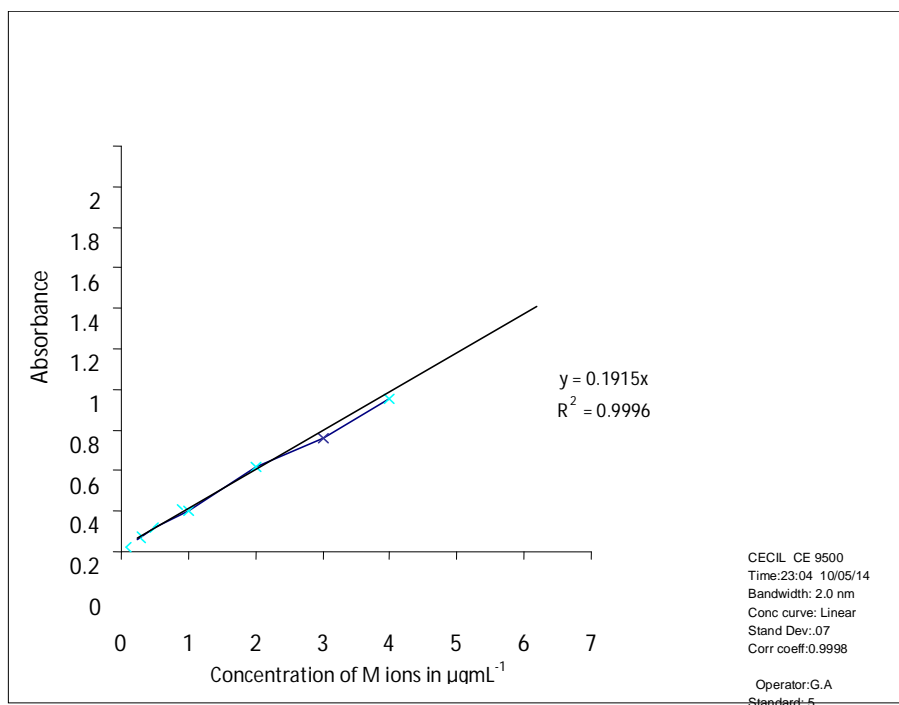


Fig. 6. Calibration graph for Cd -PAN complex in 0.02M CTAB

Table 1. Analytical parameters of Cd(II)-PAN in CTAB

Parameters	Cd(II)
Wavelength, $\square$ nm	544.86
pH	9.0
Surfactant / 0.02M CTAB / mL	1.0
PAN concentration (M)	$5.0 \times 10^{-4}$
PAN (molar excess, M:R)	1:2
Linear range $/\mu\text{g mL}^{-1}$	0.25-4.0
Molar absorption coefficient ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	$1.59 \times 10^4$
Sandell's sensitivity $/\text{ng cm}^{-2}$	7.0
Detection limit $/\mu\text{g mL}^{-1}$	0.12
Correlation coefficient ( $R^2$ )	0.9996
Reproducibility (%RSD)	0.91

Table 2. Effect of foreign ions on Cd (II) -PAN ( $\mu\text{g}$ )

Metal ion / salt	Cd(II) Remark
$\text{Na}_2\text{tartarate}$	1500
$\text{KSCN}$ , $\text{KClO}_3$	1000
$\text{NaF}$ , $\text{CH}_3\text{COO}^-$	600
$\text{Na}_2\text{citrate}$ , $\text{Pb(II)}$	500
$\text{Al(III)}$ ,	300
Bromide, Iodide, Chloride, Borate, $\text{Na}_2\text{C}_2\text{O}_4$	200
EDTA, Cyanate, $\text{Fe(II)}$ , $\text{Mn(II)}$ , $\text{Zn(II)}$ , $\text{Hg(II)}$	100 <sup>b</sup>
$\text{Cu(II)}$	10
$\text{Co(II)}$	30
$\text{Ni(II)}$	100
$\text{Cr(III)}$	50
$\text{Cr(IV)}$	8

Table 3. Determination of cadmium (II) in real samples

Sample	Metal ion	Metal ( $\mu\text{g}$ ) present	Metal ( $\mu\text{g}$ ) found	RSD %	Relative error %	Recovery %
Industrial waste water	$\text{Cd(II)}$	4.78	0.7	4.71	0.4	98.53

Table 4. % age recovery amount of Cd (II) ions added to tap water

Metal ions	Amount added ( $\mu\text{g mL}^{-1}$ )	Amount found ( $\mu\text{g mL}^{-1}$ )	Recovery (%)
$\text{Cd(II)}$	1.50	1.48	98.67

Table 5. Determination of cadmium (II) in industrial waste

Sample	Analyte ion	Proposed method $\mu\text{g mL}^{-1}$	RSD %	AAS method $\mu\text{g mL}^{-1}$	RSD %	Recovery %
Industrial waste water	Cd(II)	4.78	0.7	4.71	0.4	98.53

Table 6. Determination of cadmium (II) in stream water sample

Sample	Spiked ( $\text{ng mL}^{-1}$ )	Amount found ( $\text{ng mL}^{-1}$ )	Recovery (%)
Stream water	0.0	1.70	
	50.0	51.50	99.61

at 95 % C.L  $n = 7$

Table 7. Comparison of Cd (II) determination methods using PAN

Metal	Method	Reference
Cd	in SDS, $\epsilon$ $1.75 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ , linear concentration $0.5\text{-}4.0 \mu\text{g mL}^{-1}$ , D.L $0.12 \mu\text{g mL}^{-1}$	G. A.Shar <i>et al.</i> <sup>31,33</sup>
Cd	in CTAB, $\epsilon$ and $1.59 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ , linear concentration $0.25\text{-}4.0 \mu\text{g mL}^{-1}$ D.L $0.25 \mu\text{g mL}^{-1}$	<i>Present method</i>

Cd(II)-PAN complex at the lower concentration level as given in the table 2 <sup>28</sup>, EDTA 1mL was added, as masking agent to remove interference of Cr(IV) and Co(II) before further addition of perchloric acid. Besides this Co (II) ions interference was removed with masking agent o-phenanthroline. At higher concentration level ascorbic acid,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$  and  $\text{SCN}^-$  does not

show interference<sup>28</sup>.  $\text{Na}_2$  tartarate at  $1500 \mu\text{g mL}^{-1}$  concentration level have not shown any interference in the absorbance of the Cd(II)-PAN complex. Citrate, phosphate, fluoride, thiocyanate, fluoride, citrate and phosphates were used as masking agents to remove the interference of the foreign ions<sup>29</sup>. Tolerance limit of foreign ions is given in Table- 2.



#### 4. Conclusions

The results obtained in the determination of cadmium (II) ions were comparable with the recently reported methods, while the present method is more sensitive, and has shown significant improvement in Beer's law linear range and in the detection limit than the reported<sup>30-35</sup>. Sensitivity and selectivity of proposed method is higher than solvent extraction methods<sup>35-36</sup>. The present method is precise, sensitive, selective, reproducible simple, rapid and versatile than the reported existing spectrophotometric methods as shown in Table 7.

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