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NOVEL SPECTROCHEMICAL DETERMINATION OF CADMIUM USING 2-(BENZYLIDENEAMINO) ETHANESULPHONIC ACID

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Abstract

2-(Benzylideneamino)-ethanesulphonic acid, BA, ($C_9H_{11}NSO_3$) was synthesized by reacting taurine ($C_2H_7SO_3$) with benzaldehyde (C_7H_6O) in alkaline medium under reflux. To determine Cd in aqueous system, the BA was reacted with Cd^{2+} under specified conditions to produce BA-Cd charge-transfer complex. This complex was found to have purple colour with an absorption maximum (λmax) at 360 nm and molar absorptivity (ε) of 8.522 x 10^3 $lmol^{-1}cm^{-1}$. Beer's law is obeyed up to 6.0μg/mL. The correlation coefficient (r) is approx. 1. The optimum BA concentration and pH are found to be 0.720 % (m/v) and 12.50, respectively. The limit of detection (LOD), limit of quantitation (LOQ) and method sensitivity (MS) are estimated at 0.0736μg/mL, 0.0764μg/mL and 0.0375, respectively. The reaction time, stability of the reaction mixture and reagent blank were investigated and found to be 20minutes and 80minutes, respectively. The best order of addition of reagents is established as; BA + Cd^{2+} + NaOH + methylamine. The extent of ionic interference in this method has been quantitatively evaluated. The most tolerated ions are Ag^+, NO_3^- ($1.00 \times 10^{-1} \mathrm{molL}^{-1}$ max) and least tolerated ions are Ni^{2+}, SO_4^{2-} ($5.00\times 10^{-4} \mathrm{molL}^{-1}$ max). Recovery of cadmium from spiked water samples shows good results (99.5-106.75%). This method has also been applied to the determination of cadmium in portable and waste waters and soil sample. Results are in good agreement with those obtained by a standard method, Atomic Absorption Spectrometry.

Keywords: 2-(benzylideneamino)-ethanesulphonic acid, cadmium determination, taurine, benzaldehyde, spectrophotometry

1. Introduction

Cadmium, a trace metal, serves no known useful purposes in the body of any living organism yet has serious and varied adverse effects when it accumulates in certain organs of the body [1]. It is ranked number 7 on the Agency for Toxic Substances and Disease Registry Top 20 List [2]. The uv-vis spectrophotometry has been in general use for the last 35 years and over this period has become the most analytical instrument in the modern day laboratory [3] due to its simplicity, versatility, speed, accuracy and cost effectiveness [4].

BA binds with cadmium via the nitrogen atom lone pair and oxygen atom of the sulphonic acid[5] to form a complex compound. Complexation reactions are used in qualitative as well as quantitative analysis of metals. Metal coordination occurs when lone pair electrons from a ligand are donated to an empty orbital in a metal ion [6]. Schiff bases (of which BA is an example) are also Lewis bases and are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (CO) has been replaced by an imine or azomethine group [7]. Schiff bases are generally bidentate, tridentate, tetradentate or polydentate ligands capable of forming very stable complexes with transition metals [7].

Many transition metal complexes have characteristic colours [8]. This means that there is an absorption in the visible part of the spectrum resulting from an electron being excited by visible light from a level occupied by an electron in a molecular orbital of the complex to an empty level. If the energy difference between the orbitals capable of transition is set to ΔE, the absorption frequency (ν) is given by ΔE = *h*ν. Electronic transitions by optical prompting are broadly classified into two groups. When both of the molecular orbitals between which a transition is possible have mainly metal *d*- character, the transition is called a d-d transition or ligand-field transition, and absorption wavelength depends strongly on the ligand-field splitting. When one of the two orbitals has mainly metal character and the other has a large degree of ligand character, the transition is called a charge-transfer i.e. metal (M) to ligand (L) charge-transfers (MLCT) and ligand to metal charge-transfers (LMCT) [9],[10],[11].

Presently, the methods easily attractive for the quantitative determination of cadmium, as it is with most metals in aqueous system include: Atomic Absorption Spectrometry (AAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS). However, the operating cost of these methods has made them unaffordable in many laboratories coupled with the very skilled personnels needed. This research work tends to fill the gap, if partly, by designing and developing a new reliable, simple, fast, efficient and cheap analytical method, based on uv/vis spectrometry for cadmium in aqueous systems using 2-(benzylideneamino)-ethanesulphonic acid (BA).

2. MATERIALS AND METHODS

2.1 Chemicals and Apparatus

Taurine, benzaldehyde, methylamine, $CdCl_2.2½H_2O$, NaOH, HCl and ethanol (95%) were supplied by Sigma-Aldrich. All reagents used were of analytical grade. Jenway 3020 pH meters Uk and Jenway 671 uv/vis-spectrophotometer by Biddy Scientific Ltd, Stone Staffs, UK, were also used.

2.2 Preparation of sodium hydroxide ethanolic and Cd^{2+} stock solutions

Sodium hydroxide (4.20 g) was dissolved in 5 mL distilled water and made up to the 1000mL mark with the ethanol. The solution was allowed to stand in a tightly stoppered bottle for 24 hrs. The clear supernatant liquid was decanted into a suitable container which was later tightly closed. $CdCl_2.2½H_2O$ (0.204l g) containing 0.203l g pure salt and 0.10 g Cd was dissolved and made up to 100 mL with distilled water. This gives 1000 ppm ($\mu g / mL$) Cd^{2+} solution. The solution was then serially diluted to the required working standards.

2.3 Synthesis of 2-(benzylideneamino) – ethanesulphonic Acid

BA was prepared based on the methods of Shakir *et al.*[5], Taurine (2-ethanesulphonic acid) and benzaldehyde (1:1 molar ratio) were dissolved in the sodium hydroxide ethanolic solution. The resulting reaction mixture was refluxed for four hours. The solid precipitate was introduced into distilled water (100 mL) and made neutral pH, filtered, washed with more distilled water and dried. This was recrystallized from ethanol to give off-white crystals of BA. The yield was 67.50%.

2.4 Determination of wavelength of maximum absorption (λmax) of BA-Cd complex

The absorption spectra of the BA-Cd complex at pH 12.50 were investigated using the methods of Okolo and Okuo[12]. When the concentration of Cd^{2+} ion was 4.0 ppm ($\mu g / mL$), the solution was treated with 5 mL 3 % of BA, 3 mL of 0.50 M NaOH and 3 mL methylamine. The solution was made up to 25 mL final solution with distilled water. This was the reaction mixture (rm). A reagent blank (rb), which was the reaction mixture without the analyte (Cd^{2+}) was also prepared.

The wavelength of maximum absorption (λmax) of the rm vs rb was established by scanning from 190 nm through 570 nm in 1cm matched silica cells using the spectrophotometer.

2.4.1 Determination of optimum pH of the BA-Cd method

Reaction mixtures each containing 4.0 ppm ($\mu g / mL$) Cd^{2+} and 0.72 % (m/v) BA along with 3 mL of 0.5M NaOH and 3 mL methylamine were prepared in twenty-one separate 25-mL calibrated flasks. Each was adjusted to a given pH ranging from 3 through 13, using 1.0M of NaOH or 1.0M of HCl. The absorbance of each solution was taken vs rb at 360 nm. A plot of absorbance vs pH was made [12].

2.4.2 Determination of the effect of BA concentration on the absorbance of the BA-Cd complex

Investigation of the variation of absorbance of BA-Cd complex with BA concentration was carried out by measuring the absorbance of the usual reaction mixture solutions containing 4.0 ppm of Cd^{2+} with varying amounts of BA at 360 nm and pH 12.50. The absorbances were plotted against BA concentrations (%m/v) [12].

2.4.3 Effect of fixing pH at acidic level

The aim of this experiment was to study the effect an acidic water sample would have on the absorbance during cadmium determination using this method, and how such sample would be treated immediately after sampling before analysis. A reaction mixture containing 4.0 ppm Cd^{2+} and 0.72 % (m/v) BA was prepared alongside its reagent blank (rb). The pH was immediately adjusted to 2.25 with 1.0 M HCl. Colour development was monitored by taking the absorbance readings at intervals of 30 minutes. A plot of absorbance vs time was made [13].

2.4.4 Effect of reaction time

This determines the maximum time required for maximum colour development in the BA-Cd system. The absorbance of the rm vs rb was taken at 5-minute interval at 360 nm and pH 12.50 in matched 1cm silica cells [14]

2.4.5 Determination of the stability of rm and rb

This studies the stability of the rm and rb after maximum colour had been developed at optimum pH 12.50. The rm and rb were prepared and allowed to stand for 20 minutes for maximum colour development. The pH was adjusted to 12.50 and the absorbance readings taken at 30-minute interval at 360 nm in matched 1cm silica cells[15].

2.4.6 Order of addition of reagents

With the concentration of BA as 0.72 % (m/v), Cd^{2+} concentration of 4.0 ppm,3.0 mL of 0.5M NaOH, and 3.0mL of methylamine, all in a 25mL volumetric flask, these were made up to mark with distilled water. This was allowed to stand for 20 minutes for max colour development, then adjusted to pH 12.50. Absorbance reading vs rb at 360 nm was taken in matched 1cm silica cells. The order of addition of reagents was varied sixteen different ways to obtain the optimum order [16].

2.5 Adherence to Beer's Law

With the concentration of BA as 0.72%(m/v), various amounts of Cd^{2+} (0.5-6.0 ppm), 3 mL of 0.5M NaOH, and 3.0 mL of methylamine, all in 25-mL volumetric flasks, these were made up to mark with distilled water. The reaction mixture was allowed to stand for 20 minutes. The pH was adjusted to 12.50 with 1.0M of NaOH. The absorbance reading of each rm vs rb at 360 nm was taken, at ambient temperature, 25-30 ^{o}C [12]. A plot of absorbance vs analyte concentration was made.

Establishment of molar absorptivity (ε), correlation coefficient (r) and estimation of the equation of the linear graph are based on calculations and derivations [13].

2.6 Interference studies

The possible interfering effects of foreign ions on the analytical signal of 4.0ppm Cd^{2+} was studied using a similar procedure by Okolo and Okuo, [12]. Some of the ions chosen are constituents of major components of natural waters while others which can form ion-associate complexes, may be present as pollutants.

The criterion for the interference was fixed at ±5.0% thus concentration of foreign ions which caused relative deviation in absorbance equal to, or lower than, 5.0% were tolerated [12].

Three samples were prepared: reference sample (rs), test sample (ts) and reagent blank (rb). The reference sample (rs) was the reaction mixture (rm) containing 4.0ppm Cd^{2+}, the test sample (ts) was the reaction mixture plus the interferent, while the reagent blank was the reaction mixture without the analyle, cadmium. The rs, ts and rb were allowed to stand for 20minutes and pH adjusted to 12.5. The absorbance (A) readings were taken against the rb. The relative deviation due to the interferent was calculated using the relation:

Relativedeviation

$$= \frac{A_{\text{without interference}} - A_{\text{with interference}} \text{ x } 100\%}{A_{\text{without interference}}} \quad (1)$$

2.7 Recovery tests on BA-Cd method

This test estimates the fraction of the analyte (Cd) obtained after a standard solution of the analyte has been analysed using the proposed method. It established the effectiveness (precision and accuracy) of the method. Distilled – deionized water samples were spiked with known amounts of cadmium [0 to 6.000ppm (µg/mL)] each contained 0.72% (m/v) BA, 3mL of 0.5M NaOH and 3.0mL of methylamine all made up to final volume of 25.0mL with distilled-deionized water. The solution was allowed to stand for 20 min for max. colour development before adjusting their pH to 12.5 with 1.0M NaOH. The absorbance was taken at 360nm in 1-cm matched silica cells against the reagent blank.

Following a similar procedure as Okolo and Okuo [12], a calibration curve was prepared to cover Cd^{2+} concentration range 0-6.00ppm (0-6.00µg/mL). From the calibration curve, the Cd^{2+} concentration in each 25.0mL final volume was determined in five replicates. The standard deviation (SD), relative standard deviation (RSD), and 95% confidence limit were calculated using the relation:

$$SD = \sqrt{\frac{\sum\left(s_i - \bar{s}\right)^2}{N-1}} \qquad (2)$$

Where s_i = individual reading

$\bar{s} =$ mean of replicate readings

N = number of replicate readings

$$RSD = \frac{SD}{\bar{s}} \qquad (3)$$

$$\text{95\% confidence limit} = \bar{s} \pm \frac{t.SD}{\sqrt{N}} \qquad (4)$$

Where t = t-test.

$$\text{\% recovery} = \frac{\text{amount found}}{\text{amount added}} \times 100\% \qquad (5)$$

Recovery range of 90-120% is acceptable [17], [18].

2.8 Application of the BA- Cd method

The proposed BA-Cd method was applied to the determination of Cd^{2+} in tap water, well water, digested soil sample and domestic waste water. Each sample was analyzed in triplicates making use of a common calibration curve. In order to test the accuracy, results were compared with those obtained using a standard method: the Atomic Absorption spectrometry (AAS).

2.8.1 Limit of detection (LOD), limit of quantitation (LOQ), and method sensitivity (MS) The LOD, LOQ and MS were estimated from 10 replicate reaction mixtures, each containing 0.05µg/mL Cd^{2+}. This was the minimum concentration of the analyte that gave an analytical signal based on this method [19].

3. RESULTS AND DISCUSSION

3.1 Synthesis of 2-(benzylideneamino)-ethanesulphonic acid

The properties of the synthesized BA are presented in Table 1 and Fig.1. Table 1 shows that the synthesized 2- (benzylideneamino)-ethanesulphonic acid (BA) was of comparable quality with reference sample [5]. Particularly, the IR peak at 1613. 64 cm^{-1} (Fig.1) clearly indicates the formation of C=N functional group arising from the coupling of taurine with benzaldehyde (Rxn. 1)

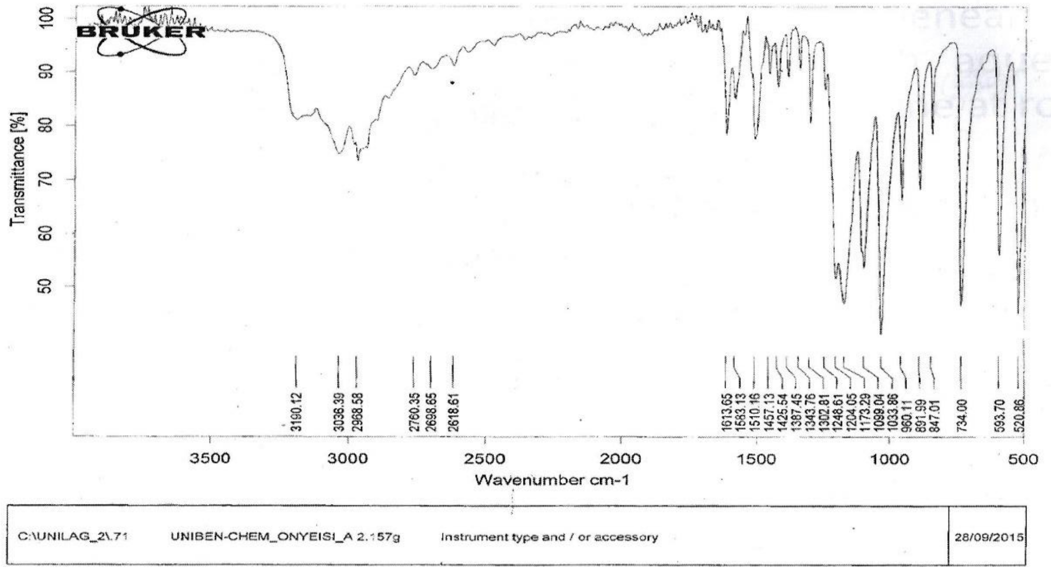
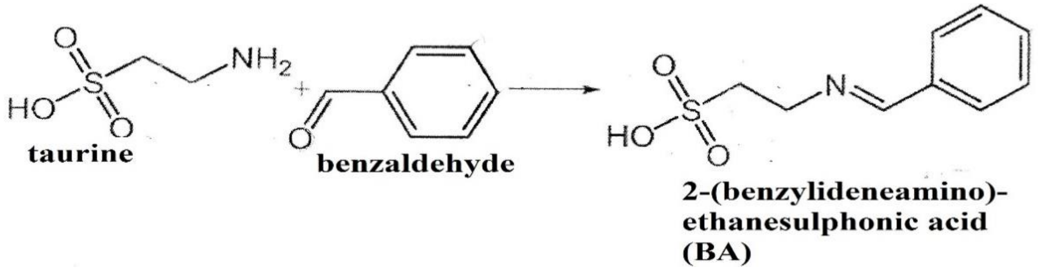


Fig. 1: IR spectra of BA

Table 1a: Characteristics of the synthesized BA as compared with literature values

Variable	**Colour**	**Melting Point (^oC)**	**λmax (uv, nm)**	**λmax (vis, nm)**	**IR(C=N) (cm^{-1})**
Literature value	Yellow	294	245	292	1614
Experimental value	Yellowish-white	294.5	240.2	291.3	1613.65



Rnx. 1

3.2. Determination of λmax for BA-Cd complex

From Fig.2 the maximum absorbance for the BA-Cd complex vs rb is at 2.079 and the corresponding wavelength (λ max) is at 360 nm. For the reagent blank (rb) vs water, the maximum absorbance is at about 0.1 which is far below the 2.079 for BA-Cd complex. This indicates that the rb does not interfere with the absorbance due to the analyte.

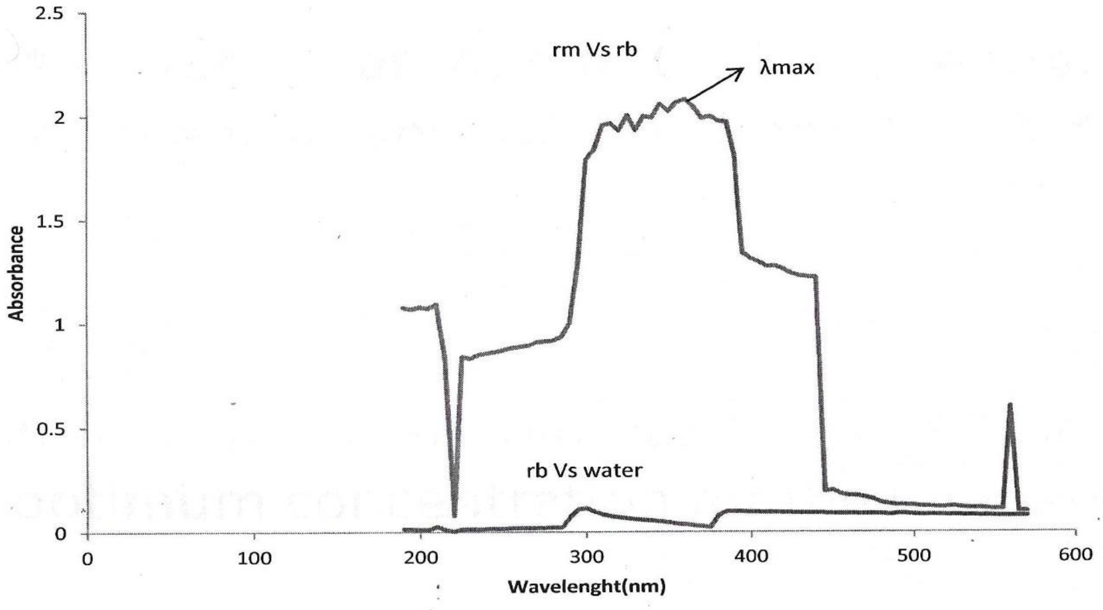


Fig. 2: Determination of λmax

3.3 Optimum pH of the BA-Cd method

At Cd^{2+} and BA concentrations of 4.0 ppm and 0.72%(m/v), respectively, and at λmax of 360 nm, the variation of absorbance with pH is shown in Fig. 3. From these, absorbance values showed prominent peaks at 0.367, 0.586 and 0.976, corresponding to the pH of 6.5, 8.5 and 12.5, respectively. Further investigations revealed that at both pH 6.5 and 8.5, the rm and rb were unstable, while the rm and rb at pH value of 12.5 were far more stable. Therefore, pH value of 12.5 was chosen as the optimum pH for this method.

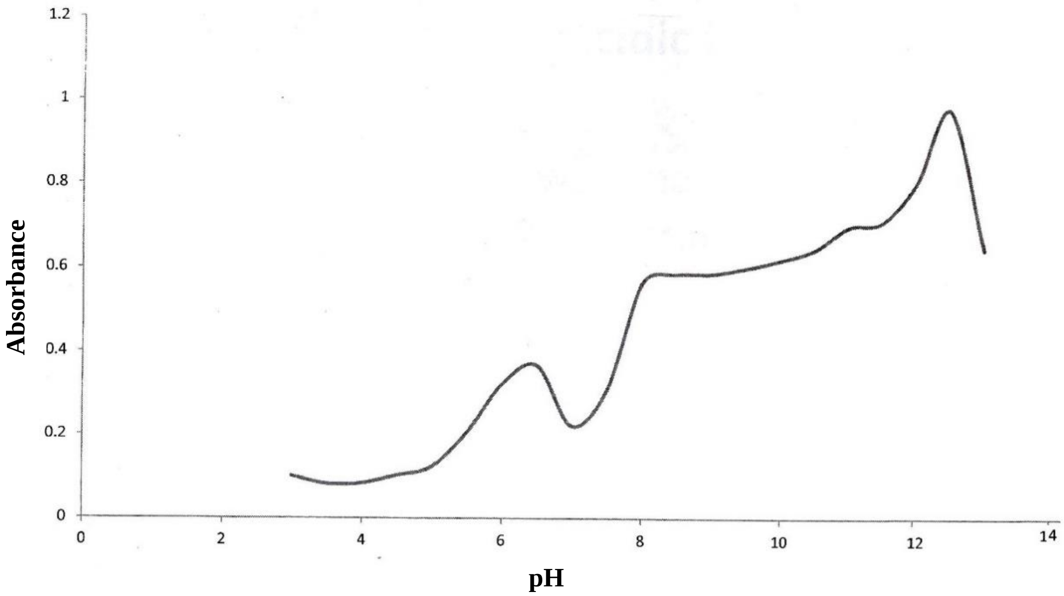


Fig. 3: Effect of pH on absorbance

3.4 Effect of BA concentration on the absorbance of BA-Cd complex

The effect of the BA concentration on the absorbance of BA-Cd complex is shown in Fig.4. and Table 1b. From the Table 1b, at 4.0 ppm Cd^{2+} concentration and varied concentrations of BA from 0.024 to 1.800%(m/v), the absorbance increased from 0.100 to a peak of 0.239 and then decreased steadily to 0.052. The BA concentration of 0.720 % (m/v) [6.0mL of 3% (m/v) BA solution in 25-mL final volume] was therefore chosen as the optimum concentration for the BA-Cd method.

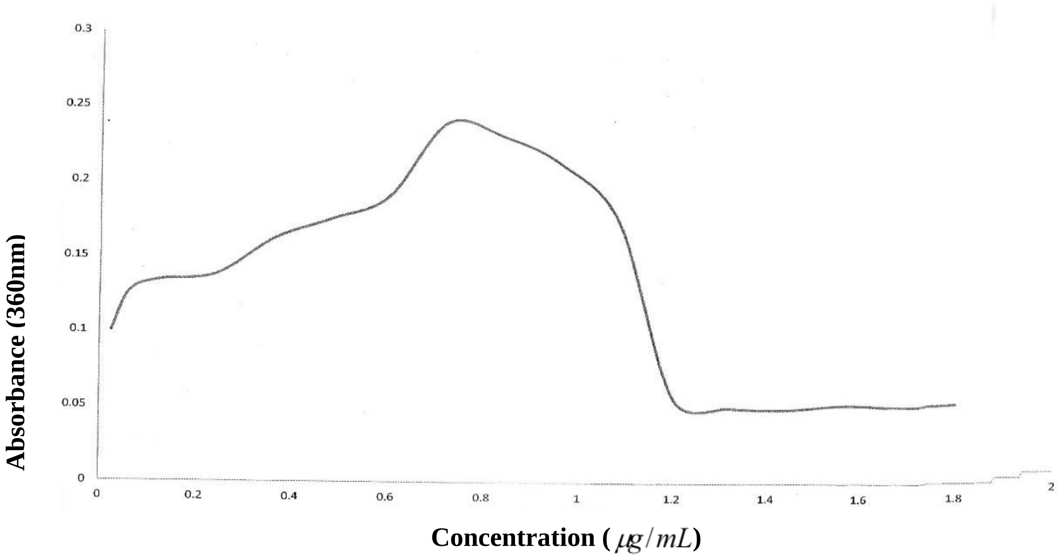
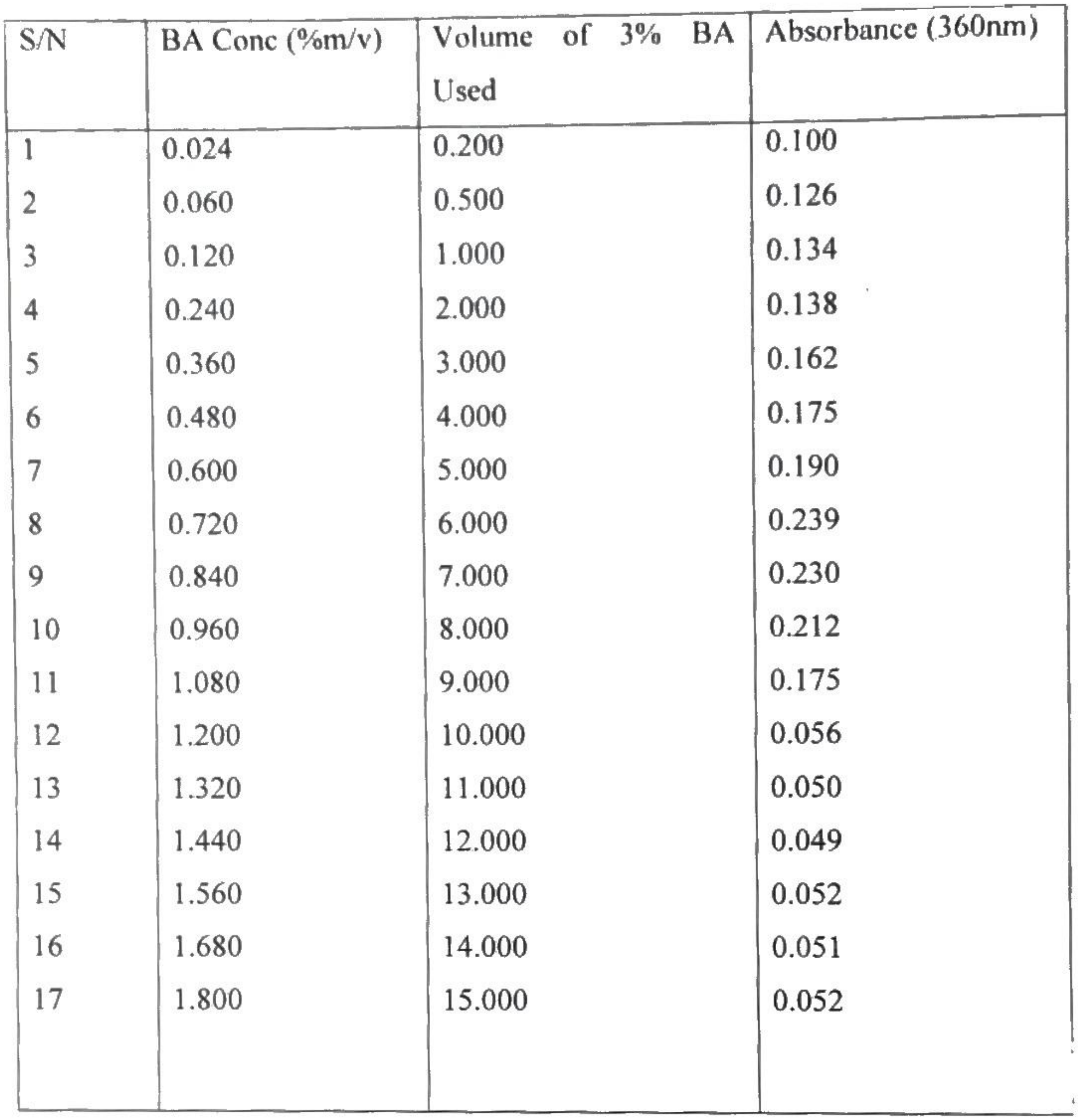


Fig. 4: Effect of BA concentration on the BA-Cd systems

Table 1b: Effect of BA Concentration on absorbance of BA-Cd system at 4ppm Cd^{2+}



S/N	BA Conc (%m/v)	Volume of 3% BA Used	Absorbance (360nm)
1	0.024	0.200	0.100
2	0.060	0.500	0.126
3	0.120	1.000	0.134
4	0.240	2.000	0.138
5	0.360	3.000	0.162
6	0.480	4.000	0.175
7	0.600	5.000	0.190
8	0.720	6.000	0.239
9	0.840	7.000	0.230
10	0.960	8.000	0.212
11	1.080	9.000	0.175
12	1.200	10.000	0.056
13	1.320	11.000	0.050
14	1.440	12.000	0.049
15	1.560	13.000	0.052
16	1.680	14.000	0.051
17	1.800	15.000	0.052

3.5 Effect of fixing pH at acidic level

The reaction mixture contained 4.0 ppm Cd^{2+} and 0.720% (m/v) BA in addition to 3.0 mL methylamine and 3.0 mL 0.5M NaOH. Fig.5 shows that acidic medium completely suppressed colour development in both rm and rb. This strongly suggests that on the collection of an acidic sample, it must first be adjusted to an alkaline pH of at least 8. The final optimum pH of 12.50 would be achieved in the process of analysis.

The reason why Cd^{2+} does not complex with the BA ligand in strongly acidic medium may be as a result of preponderance of proton (H^+) in the reaction mixture which competes with Cd^{2+} for the active sties on the BA ligand. In alkaline medium, the Cd^{2+} has excellent chances of complexing with the BA ligand via the N and O donor atoms [13].

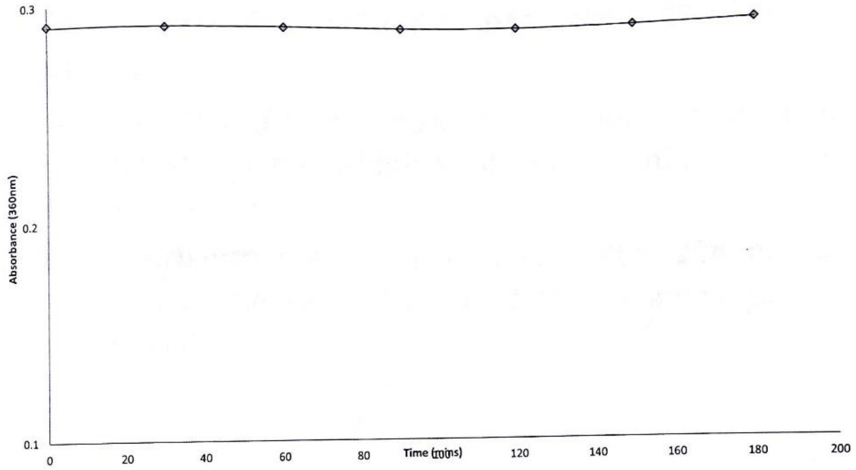


Fig. 5: Effect of fixing pH at acid level

3.6 Effect of reaction time on absorbance of BA-Cd system

Fig. 6 shows that colour developed instantaneously on addition of methylamine to the reaction mixture. The absorbance reached a maximum after 20 minutes. Therefore, 20 minutes was chosen for the maximum colour development of the reaction mixture (rm).

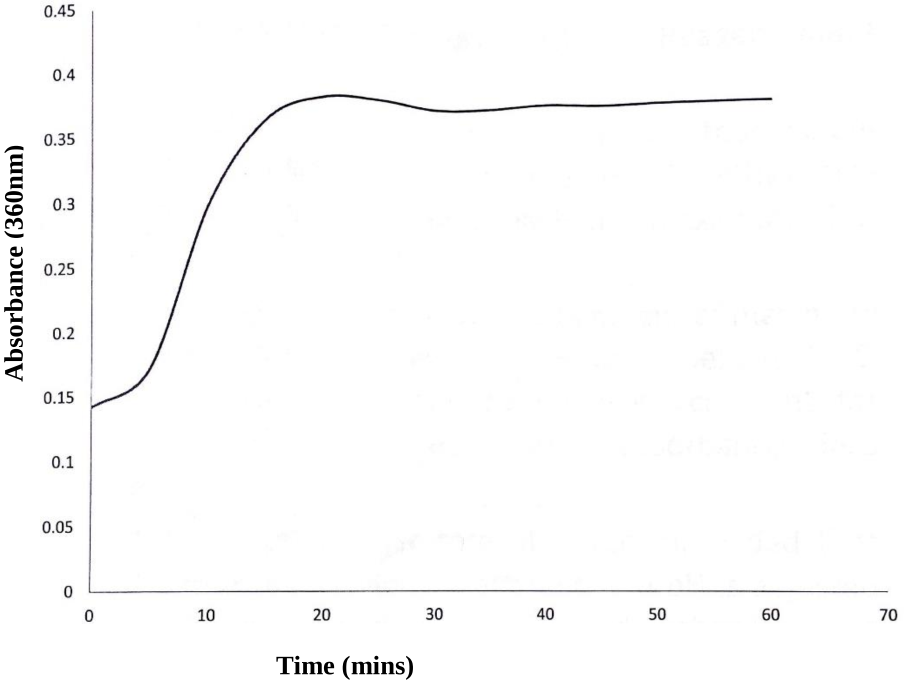


Fig. 6: Effect of reaction time

3.7 Stability of the rm and rb

Earlier, Fig.6 had shown that colour developed instantaneously after addition of methylamine during the formation of the BA-Cd complex and reached a maximum after 20 minutes. Fig. 7 indicates that after attainment of maximum colour development followed by pH adjustment to 12.5, the absorbance of rm and rb remained constant for 80minutes. After the 80 minutes, absorbance decreased gradually. From the foregoing, therefore, it is recommended that once the maximum colour is attained and pH adjusted to 12.5, the rm and rb should be used within the next 1hr 20minutes (80minutes). Thereafter the rb and rm should be discarded.

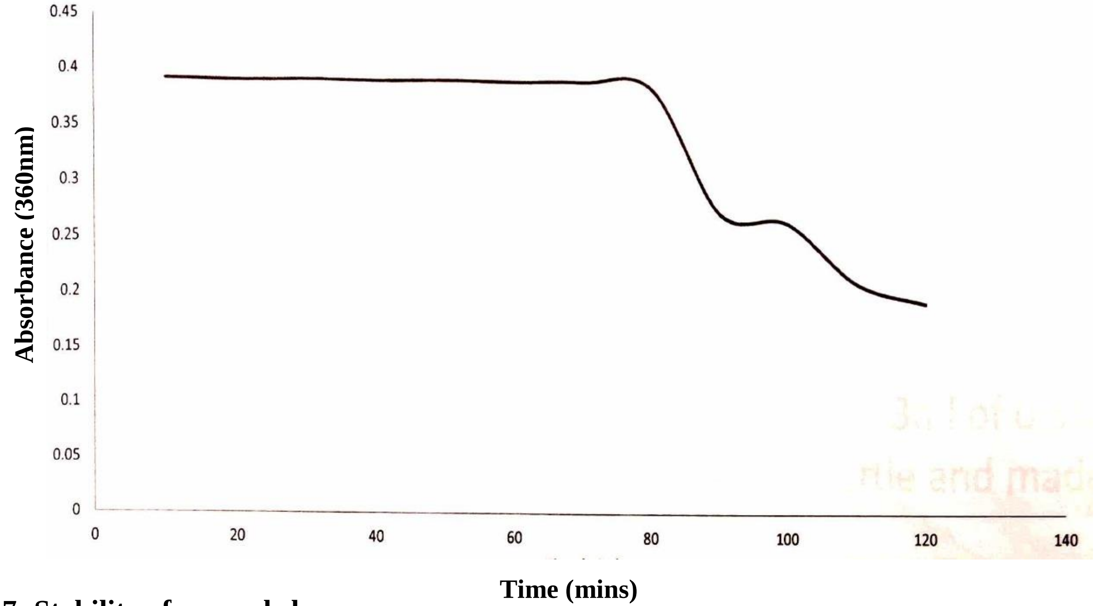


Fig. 7: Stability of rm and rb

3.8 Order of addition of reagents and adherence to Beer's Law

The effect of order of addition of reagents was studied. From the results (Fig. 8), the optimum order of addition of reagents is as follows: BA+Cd^{2+} + NaOH + methylamine. Fig 9 shows that when the recommended procedure is followed, Beer's law is obeyed up to 6.0ppm Cd^{2+}. Beyond 6.0 ppm, positive deviation is observed.

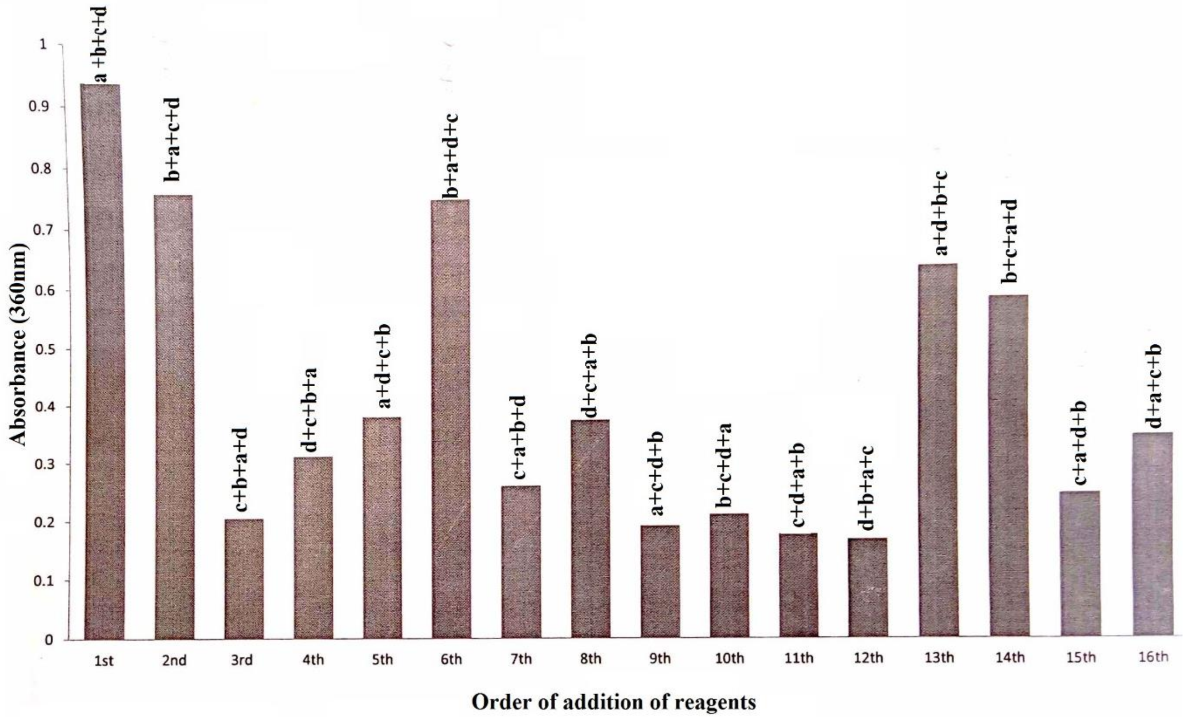


Fig. 8: Order of addition of reagents

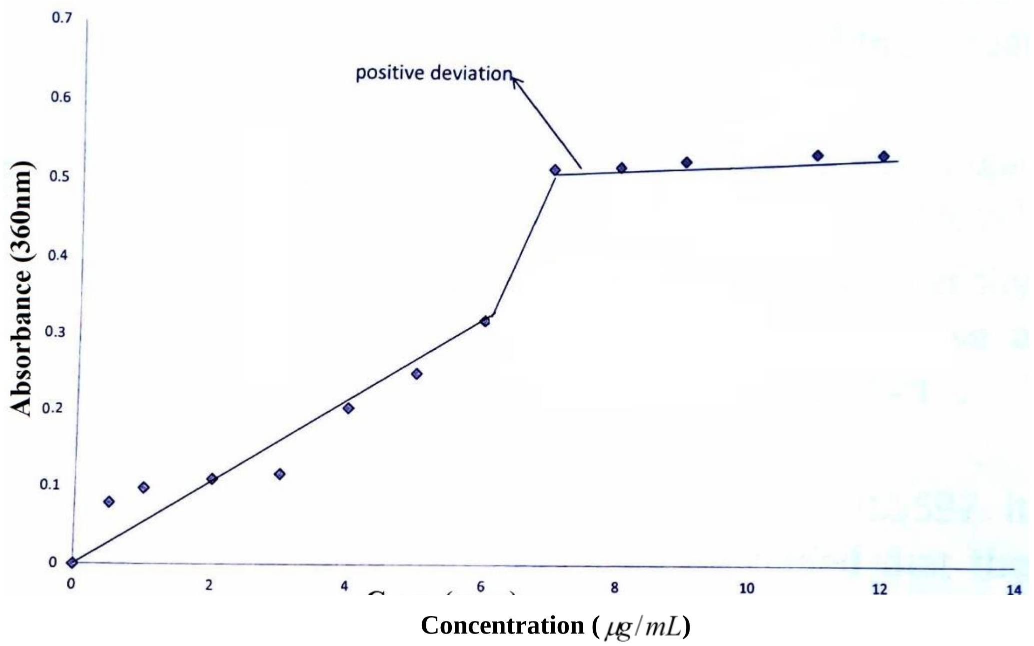


Fig. 9: Adherence to Beer's Law

3.9 Molar absorptivity (ε), correlation coefficient (r) and estimation of the equation of the linear graph.

3.9.1 Molar absorptivity (ε)

From Table 2 and Fig.10, the calculated molar absorptivity (ε) for BA-Cd complex is 8.522x10^3L $mol^{-1}cm^{-1}$. Molar absorptivity is a measure of absorption intensity of a photo-active species and the value recorded in this work indicates that the BA-Cd compound is age-transfer complex [11].

The correlation coefficient (r) as obtained from Fig. 10 is approx. 1. It is a measure of precision of the method, and can be concluded that this value reveals a high degree of correlation (linearity) between the absorbance and analyte concentration. For a perfectly linear relation, the value of r will be ±1. The value that exceeds ±0.7 indicates acceptable linearity, while values below ±0.5 are evidence of little correlation between the two variables [20].

Fig. 10 also gives the equation of the straight line graph as:

$$y = 0.1181x + 0.009 \qquad (7)$$

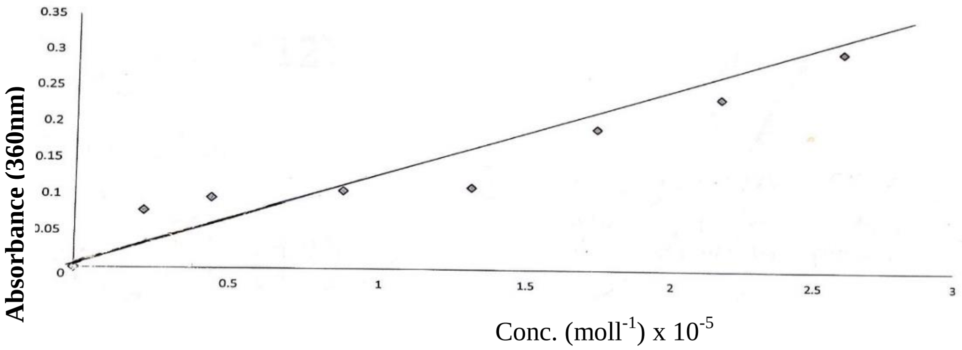


Fig. 10: Calculation of molar absorptivity

Table 2: Calculation of molar absorptivity of (ε)

Conc. of Cd^{2+}ppm	**Conc. of Cd^{2+}(moll^{-1})x10^{-5}**	**Absorbance (360nm)**
0.5	0.219	0.079
1.0	0.438	0.098
2.0	0.876	0.110
3.0	1.314	0.117
4.0	1.752	0.204
5.0	2.190	0.250
6.0	2.628	0.320

From Beer's law,

A = εbc (8)

$\varepsilon = A/bc \approx A/c$, since b= 1cm

$$\Delta A/\Delta c = \frac{0.25-0.1}{(2.190-0.4)\times 10^{-5}} = \frac{0.15}{1.76\times 10^{-5}}$$

$$\therefore \varepsilon = 8.522x10^{3}\, lmol^{-1}cm^{-1}$$

From Fig.10,

3.9.2 Correlation coefficient (r)

Based on Table 2, the Table 3 was derived for the purpose of calculating r:

Table 3: Calculation of correlation coefficient, r.

$x\times(10^{-5})$	y	$\bar{y}$	$\bar{x}$	$x_1-\bar{x}$	$y_i-\bar{y}$	$(x_i-\bar{x})(y_i-\bar{y})$	$(x_1-\bar{x})^2$	$(y_i-\bar{y})^2$
0.219	0.079			-1.126	-0.089	0.1002	1.2679	0.0079
0.438	0.098			-0.907	-0.070	0.0635	0.8226	0.0049
0.876	0.110			-0.469	-0.058	0.0272	0.2200	0.0034
1.314	0.117	0.168	1.345	-0.031	-0.051	0.0016	0.00096	0.0026
1.752	0.204			0.407	0.036	0.0147	0.1656	0.0013
2.190	0.250			0.845	0.082	0.0693	0.7140	0.0067
2.628	0.320			1.183	0.152	0.2950	1.6461	0.0231

$$\sum(x_i-\bar{x})(y_i-\bar{y}) = 0.5715; \sum(x_i-\bar{x})^2 = 4.83716; \sum(y_i-\bar{y})^2 = 0.0499$$

$$r = \frac{\sum(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum(x_i-\bar{x})^2\sum(y_i-\bar{y})^2}} \qquad (9)$$

$$r = \frac{0.5715}{\sqrt{4.83716\times 0.0499}} = \frac{0.5715}{\sqrt{0.24137428}}$$

$$= \frac{0.5715}{0.4913} \qquad = 1.1$$

Estimation of the equation of the linear graph, $y = bx + a$

When b = $\frac{\sum(x_i-\bar{x})(y_i-\bar{y})}{\sum(x_i-\bar{x})^2} = \frac{0.5715}{4.83716}$

$= 0.1181$ (10)

$a = \bar{y} - b\bar{x}$ (11)

$= 0.168 - (0.1181)(1.345)$

$= 0.168 - 0.159$

$= 0.009$

Therefore,

$y = 0.1181x + 0.009$ (12)

3.10 Interference studies

The effect of foreign ions on the absorbance when the cadmium concentration was 4.0 ppm is shown in Table 4. Some of the ions are main components of natural waters while others which can form ion-associates, could be present as pollutants, were investigated. Some of the ions include $Ca^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, CO_3^{2-}, SO_4^{2-}, Cl^{-}, NO_3^{2-}$.

The criterion for interference was fixed at $\pm 5\%$. that is, concentrations of foreign ions which cause relative deviations equal to, or lower than, 5% were tolerated. Most of the ions tested were tolerated in a wide range of concentrations.

Some of the most tolerated ions are Ag^+, NO_3^- ($1.00\text{x}10^{-1}$moll^{-1}max.) and least tolerated ions are Ni^{2+}, $SO_4^{2-}(5.00x10^{-4}moll^{-1}\text{ max}.)$

Table 4: Effect of foreign ions on the absorbance of 4 ppm Cd^{2+}

Species	Added as	Tolerated conc.(moll^{-1})	Relative deviation (%)
Ca^{2+}	$CaSO_4$	$5\text{x}10^{-4}$	3.4
Zn^{2+}	$(CH_3COO)_2Zn$	$4.0\text{x}100^{-2}$	2.6
Ni^{2+},SO_4^{2-}	$NiSO_4.6H_2O$	$1.4\text{x}10^{-4}$	-2.63
Cu^{2+},Cl^-	$CuCl_2$	$3.0\text{x}10^{-2}$	-3.715
Ag^+,NO_3^{2-}	$AgNO_3$	$1.0\text{x}10^{-1}$	-2.91
K^+,CO_3^{2-}	K^2CO_3	$5\text{ x }10^{-4}$	3.4

3.11 Recovery tests

The accuracy and precision of the proposed method were studies by spiking water samples (deionized, distilled water) with cadmium and analyzing five replicates of each. Results are shown in Tables 5 and 6. Recovery range of 90-120% is acceptable [17],[18].

a) Recovery of 0.2 μ g/mL Cd^{2+} spiked into 20mL deionized, distilled water

Fig.11 is the calibration curve for the recovery of 0.2µg/mL Cd^{2+} added to 20mL deionized, distilled water, and Tables 5a, b, c, show details used for the recovery calculation.

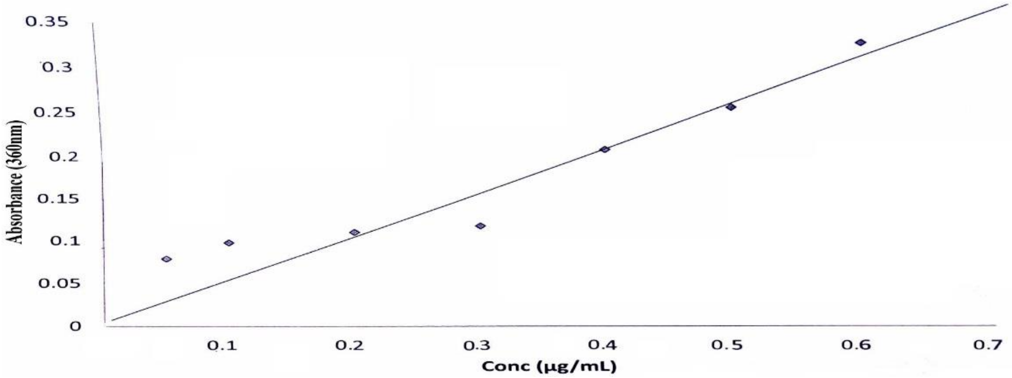


Fig. 11: Recovery of 0.2 $\mu g/mL$ Cd^{2+} added to deionized water

Table 5a: Recovery of 0.2 $\mu g/ml\ Cd^{2+}-$absorbance measurements

Replicate spiked water sample (0.2 $\mu g/ml\ Cd^{2+} added$	**Absorbance (360nm)**	**Conc. (ppm)w.r.t. 25mL final solution as red from calibr. Curve**	**Corresponding conc. (ppm) w.p.t 20mL spiked water sample**
s_1	0.082	0.170	0.2125
s_2	0.084	0.172	0.2150
s_3	0.084	0.172	0.2150
s_4	0.082	0.170	0.2125
s_5	0.082	0.170	0.2125

Table 5b: Recovery of 0.2 μ g/mL Cd^{2+} -- calculations of SD, RSD, 95% conf. limit, and % recovery

S/N	**s_i**	$\bar{s}$	$s_i-\bar{s}$	$(s_i-\bar{s})^2$	$\sum(s_i-\bar{s})^2$
1	0.2125		-0.0010	0.000001	
2	0.2150		0.0015	0.00000225	
3	0.2150	0.2135	0.0015	0.0000225	0.0000075
4	0.2125		-0.0010	0.000001	
5	0.2125		-0.010	0.0001	

$$SD=\sqrt{\frac{\sum(s_i-\bar{s})^2}{N-1}}=\sqrt{\frac{0.0000075}{4}}=0.0014$$

$$RSD=\frac{SD}{\bar{S}}=\frac{0.0014}{0.2135}=0.0066$$

95% confidence limit = $\bar{s}\pm t\frac{SD}{\sqrt{N}}$, where t = 2.78, from statistical table.

$\therefore$ 95% conf. limit = 0.2 135± $\frac{2.78x0.0014}{\sqrt{5}}$

$=0.2135\pm0.0017\mu g/ml$

$$\%\,\text{recovery} = \frac{\text{amount found x }100\%}{\text{amount added}}$$

$$=\frac{0.2135}{0.2}\times100\%$$

= 106.75%

Table 5c: Recovery of 0.200µg/mL Cd^{2+} -- summary

Cd^{2+} added $(\mu g/mL)$	Cd^{2+} recovery $(\mu g/mL)$	% recovery	SD $(\mu g/mL)$	RSD	95% conf. limit %
0.2000	0.2135	106.75	0.0014	0.0066	0.2135±0.0017

b) Recovery of 5.00 $\mu g/mL$ Cd^{2+} spiked into 20mL water

Fig. 12 is the calibration curve for the recovery of 5.000 $\mu g/mL$ Cd^{2+} added to 20mL distilled, deionized water, and Tables 6a, b, c show details used for recovery calculations

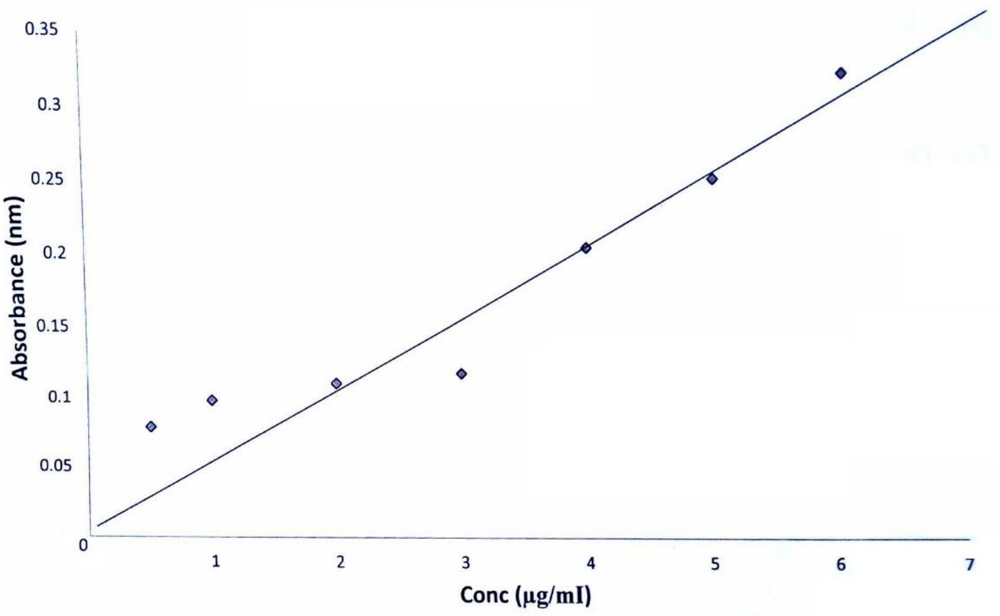


Fig. 12: Recovery 5.0 $\mu g/mL$ Cd^{2+} added to water using the BA-Cd system.

Table 6a: Recovery of 5.000 $\mu g/mL$ - absorbance measurements

Replicate spiked water sample (5.000 $\mu g/mL$ Cd^{2+} added)	Absorbance (360nm)	Conc.(ppm) w.r.t 25mL final rm soln., as red from calibr. Curve	Corresponding conc.(ppm) w.r.t 20mL spiked water sample
s_1	0.208	4.00	5.000
s_2	0.206	3.90	4.875
s_3	0.208	4.00	5.000
s_4	0.209	4.00	5.000
s_5	0.209	4.00	5.000

Table 6b: Recovery of 5.000 $\mu g / mL$ Cd^{2+}- calculations of SD, RSD, 95% conf. limit and % recovery

S/N	**s_i**	$\bar{s}$	$s_i - \bar{s}$	$(s_i - \bar{s})^2$	$\sum(s_i - \bar{s})^2$
1	5.000		0.025	0.000625	
2	4.875		-0.100	0.010000	
3	5.000	4.975	0.025	0.000625	0.0125
4	5.000		0.025	0.000625	
5	5.000		0.025	0.000625	

$$SD = \sqrt{\frac{\sum(s_i - \bar{s})}{N-1}} = \sqrt{\frac{0.0125}{4}} = 0.056$$

$$RSD = \frac{SD}{\bar{s}} = \frac{0.056}{4.975} = 0.011$$

95% confident limit = $\bar{s} \pm \frac{tSD}{N}; t = 2.78$

$$4.975 \pm \frac{2.78x0.056}{\sqrt{5}}$$

$$= 4.975 \pm 0.070$$

% recovery = $\frac{\text{amount found x 100\%}}{\text{amount added}}$

$$= \frac{4.975\mu g / ml\, Cd^{2+}}{5.000\mu g / ml\ Cd^{2+}} \times 100\%$$

$$= 99.50\%$$

Table 6c: Recovery of 5.00 $\mu g / mL\ Cd^{2+}$ -- summary

Cd^{2+} added $(\mu g / mL)$	**Cd^2 recovered $(\mu g / mL)$**	**% recovery**	**SD**	**RSD**	**95% conf. limit (%)**
5.000	4.975	99.50	0.056	0.011	4.975±0.070

3.12 Application of AAS and BA-Cd system to determine Cd^{2+} in water samples

The proposed method (BA-Cd system) was applied to the determination of Cd^{2+} in digested soil sample, running tap water, well water and domestic waste water. In order to further test the accuracy, results were compared with those obtained by the Atomic Absorption Spectroscopy. The Table 7 shows that the two methods are in agreement. Fig.13 is the calibration curve used for the BA-Cd system.

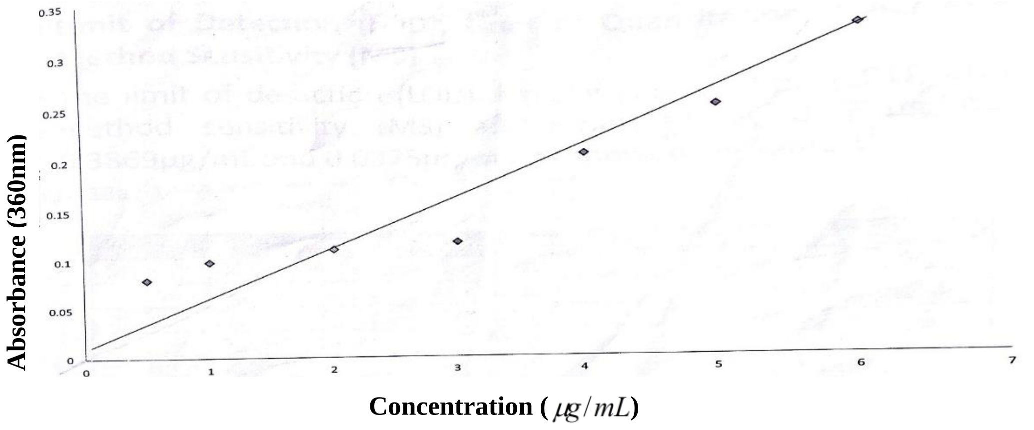


Fig. 13: Applying BA-Cd system to various water samples and a soil sample.

Table 7: Application of BA-Cd system and AAS to determined Cd^{2+} in various water samples and in a soil sample.

Sample	AAS		BA-Cd method	
	W.r.t 100mL soln (µg/mL)	W.r.t 25mL soln (µg/mL)	Absorbance (360nm)	Corresponding conc. $(\mu g/mL)$ in 25mL rm
Digested soil sample	0.500	2.000	0.105	1.920
Running tap water	0.000	0.000	0.002	ND
Well water	0.000	0.000	0.012	ND
Domestic waste	0.100	0.400	0.030	0.425

From Table 7, the AAS quantified the Cd^{2+} ion in the soil sample as 2.000 $\mu g/mL$ with respect to (w.r.t) 25mL final sample solution while the proposed BA-Cd system registered 1.920 $\mu g/mL$ w.r.t the same 25mL final sample solution. For the domestic wastewater sample, the AAS indicated Cd^{2+} ion concentration w.r.t 25mL sample solution as 0.400 $\mu g/mL$, while the proposed method yielded 0.425 $\mu g/mL$. For the the other water samples, running tap water and well water, both AAS and the proposed method showed nil for Cd^{2+} ion concentration. Overall, the two method are in good agreement.

3.13 Limit of detection (LOD), limit of quantitation (LOQ) and method sensitivity (MS).

The LOD, LOQ and MS are estimated as 0.0736 µg/mL,0.0764µg/mL and 0.0375, respectively, as calculated from Tables 8a and b

Table 8a: Data for the cal. of LOD, LOQ and MS

S/N	Absorbance (360nm)	Corresponding conc. ($\mu g/mL$) w.r.t the original 100mL	Conc.($\mu g/mL$) w.r.t the final 25mL
1	0.021	0.25	0.05
2	0.022	0.25	0.05
3	0.022	0.25	0.05
4	0.022	0.25	0.05
5	0.019	0.22	0.044
6	0.019	0.22	0.044
7	0.019	0.22	0.044
8	0.019	0.22	0.044
9	0.019	0.22	0.044
10	0.019	0.22	0.044

Table 8b: Derived data for the calculation of LOD, LOQ and MS

s_i	$\bar{s}$	$s_i - \bar{s}$	$(s_i - \bar{s})^2$	$\sum (s_i - \bar{s})^2$
0.05	0.0464	0.0036	1.296×10^{-5}	8.64×10^{-5}
0.05		0.0036	1.296×10^{-5}	
0.05		0.0036	1.296×10^{-5}	
0.05		0.0036	1.296×10^{-5}	
0.044		0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	

0.044 0.0024 $5.76x10^{-6}$

$$\delta = \sqrt{\frac{\sum (s_i - \bar{s})^2}{N-1}} = \sqrt{\frac{8.64x10^{-5}}{9}} = \sqrt{9.6x10^{-6}} = 0.003$$

$$\text{LOD} = \bar{s} + 3\delta =$$
$$= 0.0646 + 3(0.003)$$
$$= 0.0736 \mu g / mL$$

$$\text{LOQ} = \bar{s} + 10\delta$$
$$= 0.0464 + 10(0.003)$$
$$= 0.0764 \mu g / mL$$

$$\text{MS = slope of Fig. 9 } \frac{\Delta A}{\Delta conc.} = \frac{0.15}{4} = 0.0375$$

4. Conclusion

This research work was able to provide alternative method for the determination of cadmium in the range of 0 - 6.00 ppm ($\mu g / mL$) in aqueous systems. The limit of detection (LOD), limit of quantitation (LOQ) and method sensitivity (ms) are estimated as 0.0736 $\mu g / mL$, 0.0764 $\mu g / mL$ and 0.0375, respectively. It is a cheap, fast and reliable analytical method which excludes sophisticated and costly equipment. It also avoids hazardous chemicals like diphenylthiocarbazone used in the Dithiozone mothed for analyzing divalent metals [21].

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