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ADSORPTIVE STRIPPING VOLTAMMETRIC METHOD FOR THE INDIVIDUAL DETERMINATION OF Cd(II), Cu(II), Pb(II), AND Zn(II) IN VEGETABLE SAMPLES USING CALCEIN

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ABSTRACT

Adsorptive stripping voltametric method is presented for the individual determination of Cd(II), Cu(II), Pb(II) and Zn(II) in vegetable samples using calcein as a complexing agent. The purpose of this study was to obtain the optimum condition of each metal ions. The optimized experimental conditions include: concentration of 0.2 mM calcein for Cu(II) and Cd(II), 0.6 mM for Zn(II), and 0.7 mM for Pb(II); pH 6 for Cd(II) and Zn(II), pH 7 for Cu(II) and Pb(II); accumulation potential -0.4 V for Cd(II) and Pb(II), -0.6 V for Zn(II) and Cd(II); accumulation time 70 s for Cd(II), 50 s for Cu(II) and 60 s for Pb(II) and Zn(II). This method has been applied to determine relative standard deviation (RSD) were (0.39; 0.74; 1.35 and 0.41)% for Cd(II), Cu(II), Pb(II) and Zn(II) with eight replicates (n = 8) measurements of 10 µg/L Cd(II), Cu(II), Pb(II) and Zn(II); with recovery are: (99.11; 99.88; 98.76 and 99.79)%. Linear range for Cd(II) and Pb(II) (0.2 – 110) µg/L, while Cu(II) and Zn(II) (0.2 – 100) µg/L . Limit of detection (LOD) (1.3871; 0.7663; 1.4372 and 0.9831) µg/L.

Keywords: Adsorptive stripping voltammetric method, vegetable samples, calcein, complexing agent

INTRODUCTION

Several analytical methods have been reported for the quantitative determination of metals in environmental matrices, like atomic absorption spectrometry (AAS)[1-4], inductively coupled plasma optical emission spectroscopy (ICP-OES), liquid chromatography, gas chromatography (GC)[5].These techniques however usually need pre-concentration steps to achieve the appropriate selectivity and sensitivity but often only meet one of these two. Adsorptive stripping voltammetry (AdSV) was chosen as an alternative method of analysis because these are high sensitivity, low detection limit level µg/L, sample preparation is simple and easy, inexpensive infrastructure. Pre-concentration time is short, generally less than 1 minute[6-16] and suitable even when used as portable equipment[12]. Furthermore, with this method, it is possible to study the chemical species of heavy metal[13-15] which is not possible with other methods.

This paper describes an adsorptive stripping voltammetric procedure for the determination of Cd(II), Cu(II), Pb(II) and Zn(II) in vegetable samples by using bis (N,N-bis(carboxymethyl)aminomethyl)fluorescein or calcein as a complexing agent (Figure 1). Calcein widely used for fluorometric determination of metal[17], be a good analytical reagent due to the nature metallochromicnya[18], and can be applied in the determination of heavy metals in AdSV[19].

The purpose of this technique is to make more selective analysis and lower detection limits. Selectivity can be improved by choosing a selective ligand and an electrolyte solution. The detection limit is lowered by increasing the concentration of the analyte adsorbed on the working electrode surface electrodes[20-23]. Several ligands have been used for the determination of trace metals simultaneously is 8-quinolinol[26], xylinol orange[24], calcon[7,9], and alizarin[15-16] The use calcein as a complexing agent in AdSV ever done for titanium[24], aluminum and gallium[22].

In this study, we have examined the application of calcein to determine of Cd(II), Cu(II), Pb(II) and Zn(II) by AdSV on a hanging mercury drop electrode (HMDE). The method relies on the effective accumulation of the Cd(II), Cu(II), Pb(II) and Zn(II) complexes with calcein onto the HMDE. The method is extremely sensitive and selective for the determination of trace metals of Cd(II), Cu(II), Pb(II) and Zn(II) in vegetable samples and optimum results are compared with the atomic absorption spectrometric method.

The parameters studied were: the effects of calcein concentration, pH, accumulation potential, accumulation time, relative standard deviation (RSD), recovery, and a limit of detection (LOD). The method at optimum condition was applied for the direct determination of Cd(II), Cu(II), Pb(II), and Zn(II) in vegetable samples such as cabbage, eggplant, cauliflower, and broccoli.

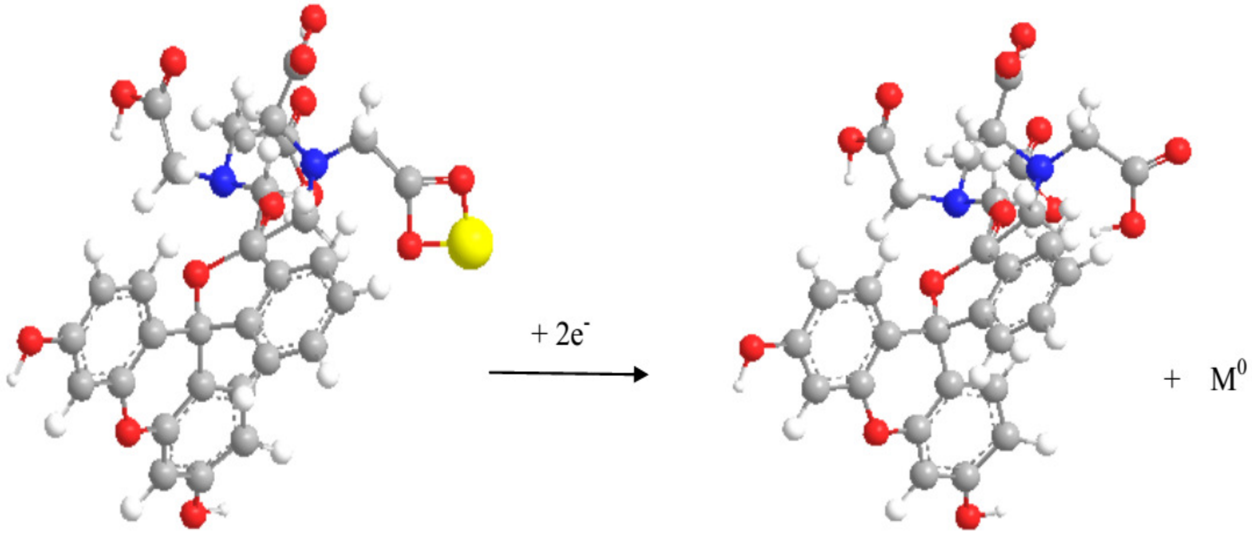

Fig.-1: Calcein-M^{+2}

EXPERIMENTAL

Material and Instruments

The materials used were: NH_4Cl, calcein, HNO_3, HCl, acetate buffer, NH4OH, nitrogen gas, doubly distilled water, Whatman filter paper and vegetable samples (cabbage, cauliflower, eggplant and broccoli.). Various chemicals were purchased from Merck and the aqueous solution of Cd(II), Cu(II), Pb(II), and Zn(II) 1000 mg/L were prepared by using the analytical grade Merck product.

The instrument used in this study were: 797 Computrance with Metrohm HMDE working electrode, are reference electrode Ag/AgCl/KCl 3M and the Pt electrode as auxiliary electrode, pH meter models 80 Griffin (Griffin & George Lough-borough, UK), analytical balance Mettler AE 200, Toledo OH-USA and glassware commonly used in laboratory.

General procedure

The purpose of this research was to obtain the optimum condition of each metal ion Cd(II), Cu(II), Pb(II), and Zn(II) by AdSV. The procedure used in this research according to the reported previously[6-16].

Samples of vegetables were used in this study are cauliflower, cabbage, eggplant, and broccoli. Before the specified metal content of Cd(II), Cu(II), Pb(II) and Zn(II) are determined once the water content, then does wet destruction with the addition of nitric acid pa and perchloric acid pa. Each sample weighed 0.5000 g carefully dried and crushed, put in a flask digestion/Kjeldahl flask. Furthermore, do wet destruction with the addition of 5 mL of concentrated nitric acid and 0.5 mL of concentrated perchloric acid, shaken and left overnight. Furthermore, heated at block digestor started with a temperature of 100°C, after the yellow steam discharged elevated temperature up to 200°C. Destruction ended when already out of white vapor and liquid in the flask remained about 0.5 mL, cooled and diluted with double distilled water and matched into a 50 mL volume, shaken until homogeneous and left overnight and filtered with Whatman 4127. The clear solution is ready determined the metal content of Cd(II), Cu(II), Pb(II) and Zn(II) with AdSV tools and AAS as a comparison.

Detection Method

Determination of the limits of detection (LOD) is done by calculating the concentration obtained from the measured peak current of each standard solution of metal ions Cd(II), Cu(II), Pb(II) and Zn(II) using optimum conditions obtained from each of the metal ions. Then calculate the average value and the standard deviation relative. The limit of detection is calculated from three times the standard deviation (3σ/B) divided by the slope of each standard solution of metal ions Cd(II), Cu(II), Pb(II) and Zn(II).

The Linear range measurement is done by measuring each peak flow of 10 mL of the standard solution of Cd(II), Cu(II), Pb(II) and Zn(II) concentrations in the range between (0 -130) µg/L at the optimum measurement conditions have been obtained previously.

RESULTS AND DISCUSSION

The Effects of Calcein Concentration

This study conducted to determine the relationship between the concentration calcein with a peak current of each standard solution Cd(II), Cu(II), Pb(II) and Zn(II) 10µg/L with accumulation potential -0.4 V for Cd(II), Cu(II), Pb(II) and for Zn(II), accumulation time of 60 s, a pH of 7 for Cd(II), Cu(II), Pb(II) and Zn(II) and the effects of calcein concentration.

From Figure-2 can be seen, the peak current for each ion Cd(II), Cu(II), Pb(II) and Zn(II) did not increase in peak current with increasing concentrations of calcein especially for metal ions Pb(II), except for Cu(II) peak current generated a significant increase in concentrations above 0.1 mM calcein. For Cd(II) and Zn(II) the highest peak currents generated at a concentration of 0.6 mM calcein medium for ions Pb(II) of 0.7 mM. This happens because there are ions Cd^{2+} and Zn^{2+} are yet to form complex compounds with calcein and at concentrations above 0.6 mM calcein decrease peak current.

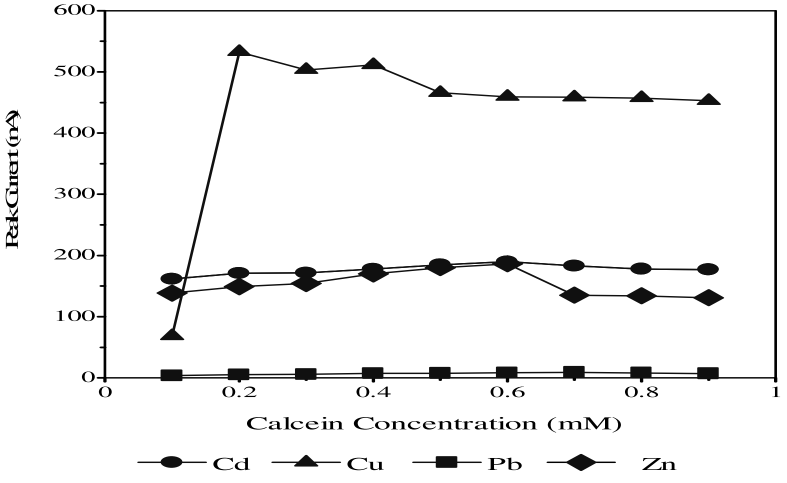

Fig.-2: Calcein concentration curves to the peak current (Ip)

Condition:
Cd: 10 µg/L; 0.2 mL Calcein; 0.2 mL KCl 0.1 M; potensial -0.4 V; time 60 s, pH 7
Cu : 10 µg/L; 0.2 mL Calcein ; 0.2 mL KCl 0.1 M; time 60 s; potensial -0.4 V; pH 7
Pb : 10 µg/L; 0.2 mL Calcein ; 0.2 mL KCl 0.1 M; time 60 s; potensial -0.4 V; pH 7.
Zn: 10 µg/L; 0.2 mL Calcein; 0.2 mL KCl 0.1 M; potensial-0.4V; time 60s; pH 7.

This condition because the competition between ligands adsorbed on the surface of the electrode in the deposition phase (pre-concentration) and form complexes with metal ions. The peak current is generated, as a result of the reduction of metal-ligand complexes are adsorbed on the surface of the working electrode to the stripping phase. The peak current generated is dependent on the concentration calcein used. The higher the concentration calcein increasingly difficult given the metal-ligand complex is reduced so that the peak current is generated is getting smaller. As for the metal ions Pb(II) an increase in the flow of nonsignificant, this is due to the formation of complex Pb-calcein not perfect so that the peak current is generated is relatively small compared to metal ions Cd(II), Cu(II) and Zn(II). The resulting peak currents increased from calcein concentration of (0.1-0.7)mM, this indicates the complex formation of Pb(II) with calcein increasing. At concentrations above 0.7 mM calcein decrease peak current, the possibility of competition between the complexing as a ligand for binding to metal ions that flow downhill. For that concentration of 0.6 mM calcein selected as the optimum conditions Cd(II) and Zn(II), 0.2 mM of Cu (II) and 0.7 mM of Pb (II). At the optimum concentration, metal ions and complexing (calcein) have completed perfectly so as to provide optimum flow.

The Effects of pH

The reaction between the metal ions Cd(II), Cu(II), Pb(II) and Zn(II) with calcein as a complexing agent influenced by the pH 8. In the AdSV, at this stage of pre-concentration reaction between the metal ion complexes with ligands, after complex formed is adsorbed on the surface of the working electrode. Reaction process described in reaction (1):

$$\mathrm{M^{n+} + nL \leftrightarrows MLn(diss)} \qquad (1)$$

$$\mathrm{MLn(diss) \rightarrow MLn(ads)}$$

At this stage of stripping, given the potential towards more negative quickly so that the metal-ligand complexes are adsorbed on the electrode is reduced forming nL^- and M^o, like reaction (2):

$$\mathrm{MLn(Hg) \quad + \; ne^- \rightarrow M^0 + nL^-} \qquad (2)$$

At the time of the reduction reaction (2), measured peak current is proportional to the concentration of the analyte in solution.

The effects pH on the complex formation between ion Cd(II), Cu(II), Pb(II) and Zn(II) ions with calcein phase deposition (pre-concentration). At the proper pH conditions is expected that more complex Cd-calcein, Cu-calcein, Pb-calcein and Zn-calcein that occur on the surface of the electrode so that it will produce an optimum peak current at the time of measurement.

The Effects pH on peak current (Ip) studied each of the standard solution Cd(II), Cu(II), Pb(II) and Zn(II) with a concentration of 10 μg/L, with a variation of pH of 3 -9. Figure-3 shows that the high peak current is influenced by the pH of each metal ion. At pH 3-7, Cu(II) and Pb(II) high peak currents generated increased, while for ion Cd(II) and Zn(II) until the pH of 6. This is due to the increasing pH solution, the more ions Cd(II), Cu(II), Pb(II) and Zn(II) in the form of free ions. As a result, the ions trapped on the surface of the working electrode and the metal complex-forming calcein, so that the resulting of peak currents increase. The pH also affects the stability of the complex formed, will also affect the concentration of the analyte deposited on the working electrode at the same peak current is generated. High peak current optimum occurs at pH 6 for ion Cd(II) and Zn(II) and pH 7 for Cu(II) and Pb(II) due to the pH of the ions are in the form of ions freely in large numbers so many ions Cd(II), Cu(II), Pb(II) and Zn(II) which is stuck on the surface of the electrode so as to form a complex with calcein[8].

At pH (7-9) peak flow has decreased, this was due to complex formation between ion Cd(II), Cu(II), Pb(II) and Zn(II) with calcein be disturbed by the presence of OH^- ions are increasingly many in solution with increasing pH. At high pH, metal ions will predominantly react with OH^- ions to form metal hydroxide so that the metal ions that react with calcein be reduced. At a certain pH, metal ions to form hydroxides and precipitate, consequently resulting current is getting smaller. Therefore a pH of 6 as the optimum pH for the determination of Cd(II) and Zn(II), while for Cu(II) and Pb(II) at pH 7.

The Effects of Accumulation Potential

The relationship between accumulation potential with peak current of Cd(II), Cu(II), Pb(II) and Zn(II) were tested on the range (-0.1 to -1.1) V. Accumulation potential is a potential at the time of the analyte deposited on the working electrode. The result can be seen in Figure-4 below.

In Figure-4, can be seen on any accumulation potential variations tested, provides peak current values are different. For metal ion Cd(II) and Pb(II) at a potential of (0.1- 0.4) (V) vs peak currents with the resulting increase, for Cu(II) on the potential range (-0.1 to -0.9) V, while for ions Zn(II) at a potential of (-0.6 to -0.1) V. This suggests a process of deposition (accumulation) analyte complex on the surface of the working electrode is maximum. At potential -0.4 V for Cd(II) and Pb(II), -0.9 V for Cu(II) and -0.6 V for Zn(II) is selected as the optimum potential for the determination of each metal ion in future studies.

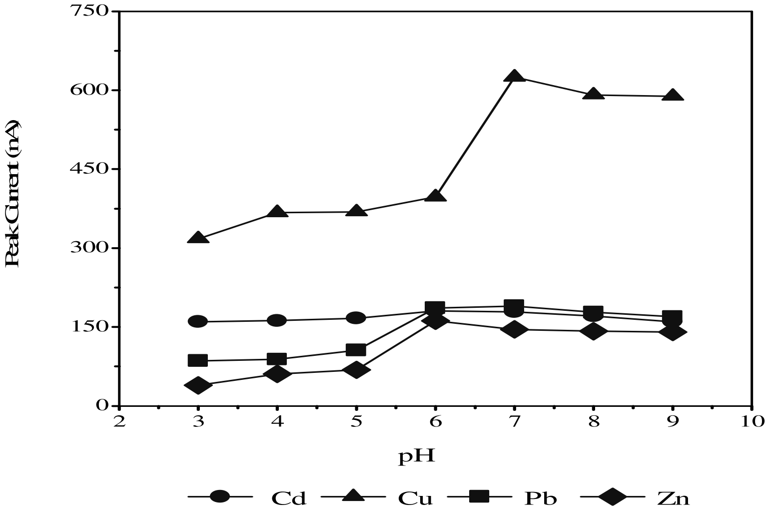

Fig.-3: pH variation curves of the peak current (Ip)

Condition:
Cd : Cd 10 µg/L; Calcein 0.6 mM ; KCl 0.1 M; time 60 s; potensial -0.4 V.
Cu : Cu 10 µg/L; Calcein 0.2 mM ; KCl 0.1 M; time 60 s potensial -0.7 V.
Pb : Pb 10 µg/L; Calcein 0.7 mM ; KCl 0.1 M; time 60 s, potensial -0.4 V.
Zn: Zn 10 µg/L; Calcein 0.6 mM: KCl 0.1 M: time 60 s, potensial -0.4 V.

The Effects of Accumulation Time

The accumulation time is the time when the analyte accumulated or deposited on the surface of the working electrode hanging mercury drops electrode (HMDE). The effects on the deposition time when the accumulation phase (pre-concentration). At this stage of the accumulated time pre-concentration useful to improve sensitivity and lower detection limits[22]. The length of time the accumulation of Cd(II), Cu(II), Pb(II) and Zn(II) affect the stability of the complex formed on the electrode surface. In this study, conducted to determine the relationship between the accumulation time with a peak flow tested, with varying time accumulated as follows: (20; 30; 40; 50; 60;70; 80; 90 and 100) s. Figure 5, shows that the long time accumulation effect on the high peak current of Cd(II), Cu(II), Pb(II), and Zn(II). High peak current increases in the accumulated time that the longer, because the ion Cd(II), Cu(II), Pb(II) and Zn(II) which accumulates and is tied with calcein on the surface of the working electrode is also more and more until it is saturated, because the entire calcein has bonded with Cd(II), Cu(II), Pb (II) and Zn(II) ions.

In measuring the accumulation time (20 – 60) s increment peak current produced is not so great, especially for a peak current of Cd(II), Cu(II). and Pb(II). This is because the ions of Cd(II), Cu(II) and Pb(II), which accumulates in the working electrode is still small. The peak current increased slightly in accumulation time (70 – 90) s. At accumulation time 90 s increased peak currents generated quite high particularly for Cu(II) and Pb(II), and used as the optimum accumulation time for subsequent determination of Cu(II) and Pb(II), while for Cd(II) 70 s. The accumulation time over 90 s does not happen again increase in the peak current, in fact, decreased. Time accumulation (deposition) longer will cause the electrode saturated.

Figure-5, accumulation time (20 – 50) s, the peak current is generated to metal ions Zn(II) is quite high when compared to the three metal ions else, meaning large enough ions Zn(II) accumulated at the working electrode so that the current the resulting peak was also great. The accumulation time over 50 s does not happen again. A peak current rise has declined. This is because the working electrode where the process of accumulation has been saturated so that a current is generated also decreased. The accumulation time of 50 s is used as the optimum accumulation time for the determination of Zn(II).

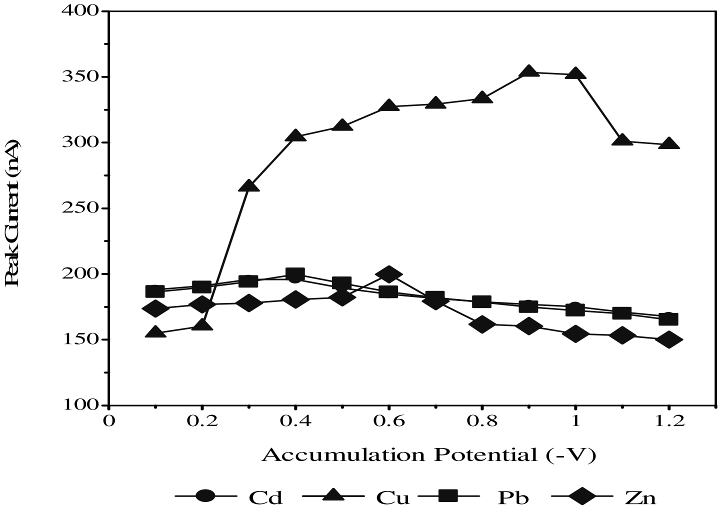

Fig.-4: Curve accumulation potential relationship to the peak current (Ip)

Condition:
Cd: Cd 10 µg/L; Calcein 0.6 mM; KCl 0.1 M; time 60; pH 6
Cu : Cu 10 µg/L; Calcein 0.6 mM ; KCl 0.1 M; time 60 s; pH
Pb: Pb 10 µg/L; Calcein 0.6 mM; KCl 0.1 M; time 60; pH 6
Zn: Zn 10 µg/L; Calcein 0.6 mM; KCl 0.1 M; time 60 s, pH 6

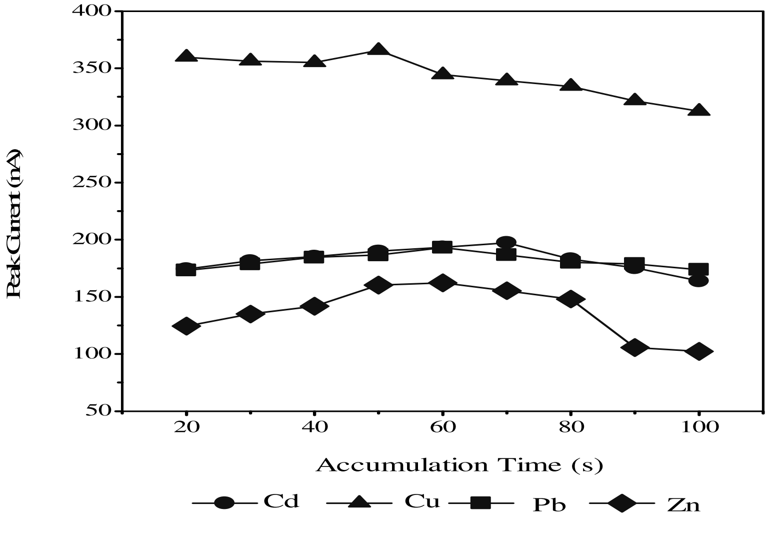

Fig.-5: Curves time accumulation of the peak current (Ip)

Condition:
Cd: Cd 10 µg/L; Calcein 0.6 mM; KCl 0.1 M; potensial -0.4V; pH 6
Cu: Cu 10 µg/L; Calcein 0.2 mM; KCl 0.1 M; potensial -0.9V; pH 7
Pb: Pb 10 µg/L; Calcein 0.7 mM; KCl 0.1 M; potensial -0.4V, pH 7
Zn: Zn 10 µg/L; Calcein 0, 6 mM; KCl 0.1 M; potensial -0.6V, pH 6

Measurement condition

The optimum condition measurement metal ion Cu(II), Pb(II), Cd(II) and Zn(II) in vegetable samples by AdSV using calcein as a complexing agent as shown in Table-1. This condition is estimated as the best conditions for the determination of metal ions Cu(II), Pb(II), Cd(II) and Zn(II) in vegetable samples.

Table-1: The determination of the optimum conditions of metal ions Cu(II), Pb(II), Cd(II) and Zn(II) by AdSV using calcein as complexing agent

Parameter	Criteria	Optimum condition			
		Cu(II)	Pb(II)	Cd(II)	Zn(II)
Suporting elektrolite	NH_4Cl, Buffer, KCl	KCl	KCl	KCl	KCl
Calcein concentration (mM)	0.1 – 0.9	0.2	0.7	0.6	0.6
pH	3 – 9	7	7	6	6
Accumulation time (s)	30 – 100	50	60	70	60
Accumulation potential (-V)	0.1 – 1.2	0.9	0.4	0.4	0.6
Drop size Mercury	3 – 9	8	8	8	8
Stirrer speed (rpm)	200 – 3000	2000	2000	2000	2000
Scan rate (mV/s)	200 – 1000	800	800	800	800

Relative Standard Deviation (RSD)

The relative standard deviation is used to see the accuracy of this method under the same operating conditions. Determining the relative standard deviation is done in the optimum condition which has been obtained above, with eight replications (n=8) measurement standard solution of each Cd(II), Cu(II), Pb(II) and Zn(II) 10µg/L are: 0.39; 0.74; 1.35 and 0.41%. According to the AOAC method28, the relative value of the standard deviation is less than 8 % at a concentration of 10 µg/L. That means these methods have a very high level of precision obtained for each metal RSD smaller than 8%.

Recovery

Recovery was used to determine the level of accuracy of this method, the number of standard solutions of known concentration is added to the sample and then compared with the concentration of samples and standards are added. In this study the use of vegetable samples to determine recovery. Results of recovery Cd(II), Cu(II), Pb(II) and Zn(II) in the adsorptive stripping voltammetry at the optimum condition, are respectively: (99.11; 99.88; 98.76 and 99.79)%. According to the AOAC method, percent recovery for a solution with a concentration of 50 µg/L is in the range of (70-110)%. That is, this method has high accuracy[28].

Linear Range and Limit of Detection

Under optimal conditions, it was found a linear relationship between the peak current with the concentration of each ion Cd(II), Cu(II), Pb(II) and Zn(II) was obtained. To verify the linear relationship between peak current and concentration of all four metal with four calibration curves were plotted under optimum conditions. Calibration equation, obtained by the method of squares is Ip = 3,936C + 161.2 (r2 = 0.986) for the determination of Cd(II), Ip = 4.327C + 303.6 (r2 = 0.988) to Cu (II), Ip = 5.012 C + 146 (r2 = 0.988) for Pb(II) and Ip = 2.521C + 113.5 (r2 = 0.985) for Zn(II), where C is the concentration of the metal ion (µg/L), and Ip is the peak current (nA). Stripping current peaks complexes Cd-calcein, Cu-calcein, Pb-calcein and Zn-calcein found proportional to the concentration of each of Cd(II), Cu(II), Pb(II) and Zn(II) in the range of (0.2-135.0; 0.2-110.0; 0.2-100.0; 0.2 - 110.0) µg/L. The limit of detection is calculated from three times the standard deviation of the reference solution divided by the slope (3σ/B) under optimum conditions, which gained the detection limit respectively: (1.021; 0.987; 0.972 and 0.957) µg/L for Cd(II), Cu(II), Pb(II) and Zn(II).

Effects of other Cations and Anions

Possible interference by other metals with the AdSV of Cd(II), Cu(II), Pb(II) and Zn(II) were investigated by the addition of the interfering ion to the solution of this metal using the optimized conditions. Based on the results, it was found that most of the foreign ions did not interfere for Cd(II), Cu(II), Pb(II) and Zn(II) determination (Table 2).

Table-2: Tolerance ratio of interfering ions in the determination of 10 µg/Lof Cd(II), Cu(II), Pb(II) and Zn(II)

Interfering ions	Tolerance limit (mg/L)			
	Cu	Pb	Cd	Zn
Na^+, Al^+, Ca^+, Li^+, K^+, Ba^{2+}, Cr^{+3},Co^{2+}, Ni^{2+}, Cl^-, F^-, Br^-, SO_4^{2-}, I^-	10	10	10	10
Cu^{2+}	-	10	1	1
Pb^{2+}	10	-	10	10
Cd^{2+}	10	10	-	10
Zn^{2+}	1	1	10	-
Fe^{3+}	1	1	1	1

Application Method

To evaluate the validity of the proposed method for the analysis of real samples, the proposed procedures applied to different samples of vegetables. The concentration of Cd(II), Cu(II), Pb(II) and Zn(II) in samples of vegetables were determined by standard addition method using the procedures recommended in optimum condition. The results in Table 3 show that the AdSV provide satisfactory results when compared to the method of Atomic Absorption Spectrophotometer (AAS).

Table-3: Comparison of the method of determination of Cd(II), Cu(II), Pb(II) and Zn(II) in theVegetable samples

Vegetable Samples	AdSV (mg/L)				AAS (mg/L)			
	Cd(II)	Cu(II)	Pb(II)	Zn(II)	Cd(II)	Cu(II)	Pb(II)	Zn(II)
Broccoli	3.764	3.781	3.219	2.712	0.926	1.161	0.888	1.238

CONCLUSION

It can be concluded that optimum conditions of the measurement of each ion metals in AdSV are: concentration calcein optimum for Cu(II) 0.2 mM, Cd(II) and Zn(II) 0.6 mM, Pb(II) 0.7 mM, at pH 6 for Cd(II) and Zn(II), pH 7 for Cu(II) and Pb(II), accumulation potential -0.4 V for Cd(II) and Pb(II), and accumulation potential -0.6 V for Zn (II); accumulation time Cd(II) 70 s, Cu(II) 50 s, Pb(II) and Zn (II) 60 s. In optimum conditions were obtained standard deviation with 8 repetitions (n = 8) on the measurement of each standard solution Cd(II), Cu(II), Pb(II) and Zn(II), 10 µg/L are: (0.39; 0.74; 1.35 and 0.41)% with recovery are: (99.11, 99.88, 98.76 and 99.79)%, with a detection limit for Cd(II), Cu(II), Pb(II) and Zn(II) respectively: (1.02; 0.99; 0.97 and 0.96) µg/L. Tolerance limit selectivity method for the determination of Cd(II), Cu(II), Pb(II) and Zn(II) to interference of other ions is 10 mg/L, and the proposed method has been successfully applied to vegetables samples.

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