Full Paper

Simultaneous Determination of Cu, Pb, Cd, AND, Zn In Tap Water Samples in the Presence of Alizarin: Differential Pulse Adsorptive Stripping Voltammetry

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Abstract- Research on the determination of Cu, Pb, Cd, and Zn metal ions in the amount of traces simultaneously using the method of Differential Pulse Adsorptive Stripping Voltammetry with alizarin as a complexing agent (DPAdSV-AZ) was performed. This study aims to obtain the optimum conditions in determining the concentration of Cu, Pb, Cd and Zn metal ions simultaneously in the amount of traces. The optimum conditions of the DPAdSV-AZ method are pH 6, AZ concentration 0.6 mM, accumulation potential -0.15 V, accumulation time 70 s. RSD for Cu, Pb, Cd and Zn are 0.22%; 0.93%; 0.39%; 0.86%, performed 10 replicates (n=10). This method was applied to tap water samples from laboratory Central Measurement Department of Chemistry, Andalas University. The concentrations of each Cu, Pb, Cd and Zn metal in the tap water sample were (5.863±13)µg/L; (0.113±32)µg/L; (18.998±6)µg/L and (121.301±22)µg/L, with AAS method obtained metal concentration of Cd and Zn is (16.000±43)µg/L and (115.200±34)µg/L, Cu, and Pb are undetectable. Recovery of each Cu, Pb, Cd and Zn metal is (98.71; 104.21; 97.60; 99.67)% and LOD metals Cu, Pb, Cd, and Zn are (0.0054; 0.0090; 0.0057, and 0.0024)µg/L. Effect of foreign ions to ion Co^{2+} and Ni^{2+} 10 mg/L disrupt the metal ions Cd and Zn, Fe^{3+}, and Cr^{6+} 5 mg/L interfere with the metal ion Zn and K^+ 10 mg/L interfere in Cu, Pb, Cd and Zn metals. The comparison DPAdSV-AZ method with AAS method for Cd and Zn metal the calculated t-test statistical value were less than the critical value (*p*=0.05) so that the two methods were not significantly different.

Keywords- (Cu, Pb, Cd, and Zn), Tap water, Alizarin, Differential pulse adsorptive stripping voltammetry

1. INTRODUCTION

Copper (Cu), lead (Pb), cadmium (Cd) and zinc (Zn) can be present in the body of water naturally and as a result of human activity. Pb and Cd are two of three highly toxic heavy metals (other than mercury). If the handling of the waste is not managed properly, it will be able to be a very bad impact on the environment [1]. Pb and Cd cause poisoning, showing adverse effects on the kidneys, liver, heart, blood vessels and the immune system. Additionally, Pb and Cd causing chromosomal abnormalities, skin allergies, cancer and miscarriages in pregnant women [2-4]. The main anthropogenic sources are the elements of fuel combustion, industrial emissions, chemical varnishes, and dyes. Cu and Zn metals are essential metals. But if the amount in the body past the threshold, it will be toxic [5]. The tolerance limit of Cu, Pb, Cd, and Zn each is (2; 0.01; 0.003, and 3) mg/L [6-7]. Therefore a simple, sensitive, selective and inexpensive method is needed for continuous determination and monitoring of heavy metals in food and water samples.

Methods for analysis of metal ions such as the method of Atomic Absorption Spectrometry (AAS) [8-9], Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [10-13], the method of Inductively Coupled Plasma Atomic Optical Emission Spectrophotometry (ICP-OES) [14-15], Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) [16-17]. However, this method is costly for routine operations, and maintenance costs are quite expensive [18-19]. Therefore, an alternative method is needed which can overcome the limitations of the method. Differential pulse adsorptive stripping voltammetry (DPAdSV) is chosen as an alternative method because it has many advantages, among others, capable of determining analytes in high salinity samples, excellent sensitivity, detection limits on ng/L scale (ppt), easy sample processing, analysis is very high, the analyte can be determined simultaneously (4-6 metals), prices are cheap infrastructure [20-33].

Alizarin (AZ) as the complexing agent has been done for the determination of metals Zn by Method square wave adsorptive stripping voltammetry (SWAdSV) [35], preconcentration in ICP-OES[36], preconcentration on FAAS[37], But only able to analyze metals in a single state and the detection limit is still high on the scale of μg/L to scale of mg/L. Therefore, the study used Alizarin as a complexion with the DPAdSV-AZ, so it can determine the metals Pb, Cd, Zn, and Cu simultaneously in a trace amount.

2. EXPERIMENTAL DETAIL

2.1. Apparatus

DPAdSV measurements were carried out with 797 AV computrace (Metrohm, Herisau, Switzerland) in connection with Dell computer and controlled by (VA computrace 2.0) control software. Stripping voltammograms were obtained via a Hewlett-Packard laser jet printer. A conventional three electrode system was used in the hanging mercury drop

electrode (HMDE) mode. This three electrode system was completed by means of a platinum auxiliary electrode and an Ag/AgCl (3 M KCl) reference electrode. A Chem Tech Analytical Model CTA-2000 Atomic absorption spectrometer (Shimadzu) was used for Cu, Pb, Cd, and Zn determination. The pH was measured with Metrohm 744 pH meters. Oxford adjustable micro-pipette (Ireland) was used to pipette microliter volumes standard solutions.

2.2. Reagents

The materials used for this study were: Alizarin (AZ), concentrated HNO3 65%, 0.01 mol/L acetate-acetic acid buffer (pH 3-6) and 0.01 mol/L phosphate buffer (pH 7-9), nitrogen gas, doubly distilled Water, What man filter paper. Various chemicals were purchased from Merck and the aqueous solution of Cu, Pb, Cd and Zn 1000 mg/L were prepared by using the Analytical Grade Merck Product. The sample used is taken from the tap water laboratory central measurement Chemistry Faculty of Mathematics and Natural Science, Andalas University.

2.3. Procedure

The general procedure for the determination of Cu, Pb, Cd and Zn metals simultaneously with the DPAdSV-AZ method was as follows: 10 ml samples were fed into a voltammeter vessel, added 0.2 ml buffer pH (3-9), and 0.2 ml AZ (0.1- 0.9) mM) as the complexing agent. The accumulation potential (-0.05 to -0.7) V, accumulation time (30-100) s is set to voltammeter.
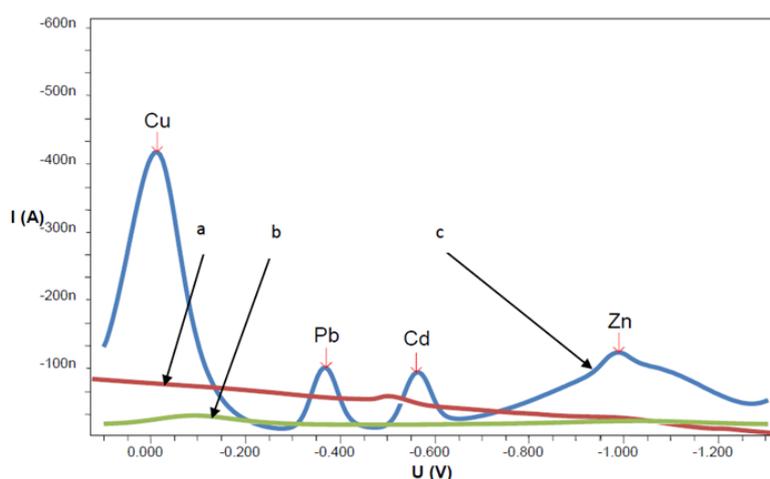

Fig. 1. Voltammogram DPAdSV-AZ without metals Cu, Pb, Cd, and Zn (a); Voltammogram of Cu, Pb, Cd, and Zn metals do not use alizarin (b); Cu, Pb, Cd, and Zn were added 0.2 ml AZ 0.6 mmol/L (c); Measurement conditions: Cu, Pb, Cd, and Zn metals were 0.01µg/L, pH

6, accumulation time 60 s, accumulation potential -0.2 V and scan potential from (-0.1 to -1.23)V

The solution was purged for 300 s using nitrogen and was stirred. After purged 300 s, preconcentration stage occurs at accumulation potential -0.15 V versus Ag/AgCl and stirred for 60 s. Stripping phase occurs after preconcentration stage is completed and after 10 s stage elapsed. The Potential scans performed in the range from (0.0 to -1.1)V. The sample used was taken from tap water of Central Laboratory, Department of Chemistry, Andalas University added HNO_3 65% (comparison with 1 ml of HNO_3:1000 ml samples).

3. RESULTS AND DISCUSSION

3.1. Effects of complexing agent (AZ)

The influence of alizarin complex versus peak current (Ip) for Cu, Pb, Cd, and Zn with accumulation potential -0.2 V, accumulation time 60 s, 0.2 mL Alizarin 0.6 mmol/L, pH 6 were studied. The result can be seen in Fig.1.

The purpose of adding the compiler is to make the analysis more selective and lower the detection limit. Selectivity can be improved by selecting ligands, the more selective the ligands the selectivity will be better. The detection limit was decreased by increasing the concentration of the adsorbed analyte on the electrode surface [33]. Figure 1 can be seen AZ 0.6 mmol/L voltammogram showing no peak current that appears in the potential area of half-cells of Cu, Pb, Cd, and Zn (a) metals.
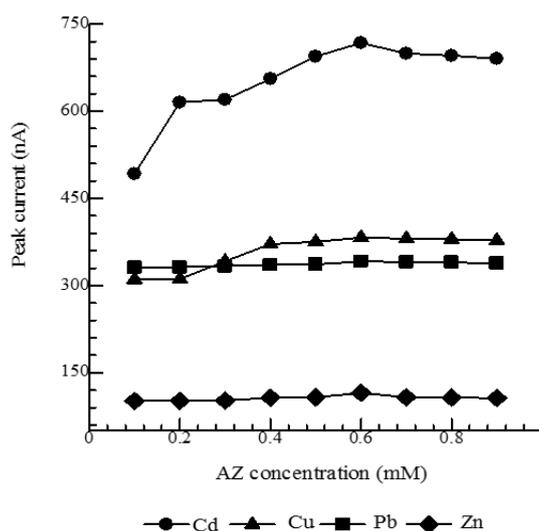

Fig. 2. Effect of AZ concentration on DPAdSV-AZ signal of Cu, Pb, Cd dan Zn respectively 0.01 µg/L in pH 6, accumulation time 60 s, accumulation potential -0.1 V and scan potential from (-0.1 to -1.23) V

This shows with the addition of AZ, does not interfere with the measurement of Cu, Pb, Cd, and Zn metals. Before AZ was added, the metals Cu, Pb, Cd, and Zn of 0.01 µg/L each produced no peak current (b). While in addition of AZ obtained peak current for metal Cu, Pb, Cd, and Zn (c). This shows that AZ can increase selectivity and decrease LOD of DPAdSV method.

3.2. Effects of AZ Concentration

The determination of the optimum condition of the complexing concentration of the standard solutions of Cu, Pb, Cd, and Zn 0.01 µg/L metals was measured under accumulation potential conditions -0.1 V, accumulation time 60 s and pH 6. The variation of AZ concentration in the test solution was from 0.1 mmol/L to 0.9 mmol/L. The results can be seen in Fig. 2.

Fig. 2 shows the origin of the current decreasing and increasing with increasing AZ concentration below 0.6 mmol/L. This is because there are still Cu, Pb, Cd, and Zn metals that have not formed complex compounds with AZ. The AZ concentrations above 0.6 mmol/L peak current value did not show a significant increase.
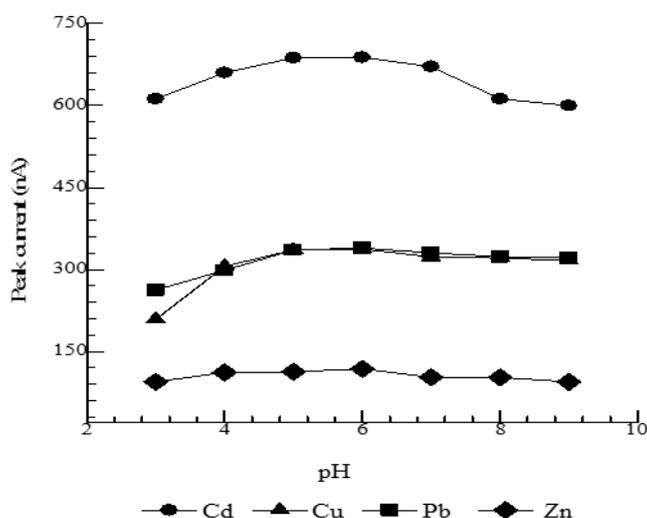

Fig. 3. Effect of pH on DPAdSV-AZ signal of Cu, Pb, Cd dan Zn respectively 0.01 µg/L in accumulation time 60 s, accumulation potential -0.1 V, AZ concentration 0.6 mmol/L and scan potential from (-0.1to -1.25) V

This is due to the competition between ligands adsorbed on the electrode surface and form complexes with metal ions [19]. Cu and Cd metals showed significant peak increases in AZ (0.1 to 0.6) mmol/L and decreased again in AZ (0.6 to 0.9) mmol/L, but the metals Pb and Zn did not show significant increase in current from AZ (0.1 up to 0.6) mmol/L and

slightly decreased to AZ 0.9 mmol/L, and the best flow of the four metals was at 0.6 mmol/L AZ, was chosen as the optimum condition.

3.3. Effect of pH

pH plays a role in increasing the number of complex compounds or associated ions formed on the adsorption process at the HMDE electrode and affecting its stability.

Fig. 3 shows the effect of pH on the peak current (Ip) on the analysis of Cu, Pb, Cd and Zn metals obtained optimum conditions at pH 6. At pH 6 this formed a stable complex between Cu, Pb, Cd and Zn metals with alizarin and formed associations Ions in large quantities so as to increase peak currents. pH smaller than 6 smaller peak currents because there are still excess protons that can compete with Cu, Pb, Cd and Zn metal forming other complexes. Conversely, a pH greater than pH 6 to be impaired due to their peak currents OH^- ions causing metal ions to form hydroxides so that the currently measured decreases [19]. pH 6 is selected as the optimum condition in the next analysis.

3.4. Effects of accumulation potential

This research is done to determine the relationship between accumulation potential and peak current tested in the range from(-0.05 to -0.7) V. The results can be seen in Fig. 4.
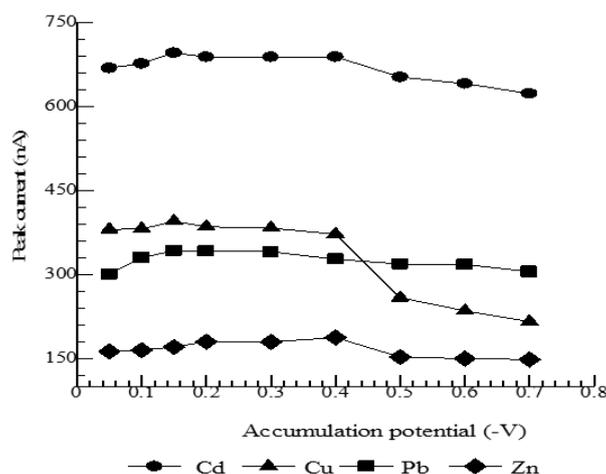

Fig. 4. Effect of accumulation potential on DPAdSV- AZ signal of Cu, Pb, Cd dan Zn respectively0.01 µg/L in pH 6, accumulation time 60 s, AZ concentration 0.7 mmol/L and scan potential from (-0.1 to -1.23) V

The accumulation potential is potential when the analyte is deposited on the working electrode. Fig. 4 shows on each variation of Accumulation potential tested, giving different peak current values. The accumulation potential from (-0.05 to -0.15) V curve rises

significantly, it states that there is a process of deposition of the analyte complex on the surface of the working electrode that has not reached the maximum. The Potential range from (-0.15 to -0.7) V for Cu, Pb, Cd, and Zn curves down, This is due to the complex reduction process of the analyte during the deposition process so that the peak current obtained at the measurement becomes decreased. The Zn metal of the (-0.15 to -0.4) V potential increases the peak current, but not so significantly, so for the determination of the Cu, Pb, Cd, and Zn metals simultaneously, the accumulated potential for the deposition of the analyte complex at the maximum working electrode surface at -0.15 V. The accumulation potential -0.15 V is used in subsequent determination.

3.5. Effect of Accumulation Time

The accumulation time with peak current is tested by varying the time from (30–100) s (fig. 5). Accumulation time is the time at which the analyte accumulates or is deposited on the working electrode surface in the form of the hanging mercury drop electrode (HMDE). The accumulation time has an effect on the accumulation stage (preconcentration). Preconcentration stage accumulation time is useful to increase sensitivity and lower LOD. The length of time the accumulation of Cu, Pb, Cd, and Zn metals affects the complex stability formed on the electrode surface. Fig. 5 shows the time duration of accumulation effect on high peak current Cu, Pb, Cd, and Zn. Higher peak currents are increasing at an accumulated time, as Cu, Pb, Cd, and Zn are accumulated and bonded with alizarin on the surface of the working electrode as well until more saturated. Since all alizarin has bound to Cu, Pb, Cd, or Zn. The results can be seen in Fig. 5.
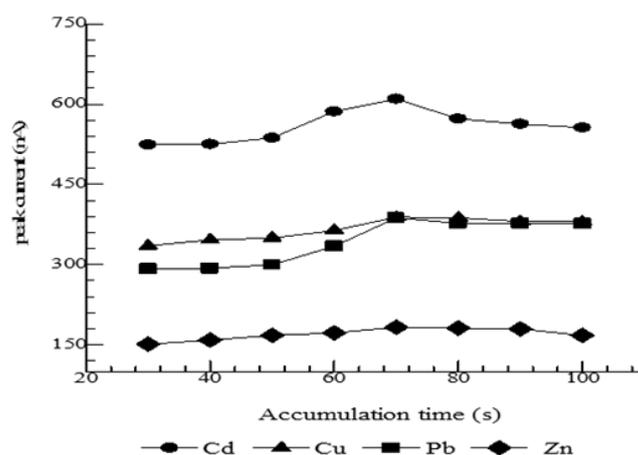

Fig. 5. Effect of accumulation time on DPAdSV-AZ signal of Cu, Pb, Cd and Zn metal solution respectively 0.01 µg/L in pH 6, accumulation potential-0.15 V, AZ concentration 0,6 mM and scan potential from (-0.1 to -1.23) V

Fig. 5 can be seen from accumulation time (30–70) s current of the peak increases linearly. Time 70 s is used as the optimum accumulation time in the next determination, because after that there is no longer peak current rise, even decreased, deposition longer will cause the saturated mercury film [19].

3.6. Relative Standard Deviation (RSD)

RSD is used to get the accuracy of a method under the same operating conditions in a short time interval. The determination of RSD was done at the concentration of Cu, Pb, Cd, and Zn metal solution respectively 0.01 µg/L with 10 replicates (n=10), the result can be seen in Table 1.

Table 1. Measurement Results of Standard Solutions Cu, Pb, Cd, and Zn 0.01µg/L

Repetition	Peak current (nA)			
	Zn	**Cd**	**Pb**	**Cu**
1	93.79	512.65	318.89	806.50
2	92.80	513.99	318.65	805.65
3	93.23	513.78	327.60	805.76
4	92.29	515.87	324.47	809.54
5	93.15	512.51	321.75	804.17
6	94.74	512.92	321.54	803.51
7	92.43	517.57	320.77	806.34
8	92.60	511.22	317.58	805.40
9	93.22	511.02	318.90	804.59
10	94.50	513.22	321.50	803.42
Average	93.27	513.48	321.16	805.49
SD	0.80	2.00	3.00	1.80
RSD	0.86%	0.39%	0.93%	0.22%

Table 1 shows the average peak currents of Cu, Pb, Cd, and Zn in sequence (805.49; 321.16; 513.48, and 93.27)nA, standard deviation of (1.80; 3.00; 2.00 and 0.80), RSD for standard solutions of Cu, Pb, Cd, and Zn 0.01 µg/L metals are obtained respectively (0.22; 0.93; 0:39, and 0.86)% and the limit of detection (3×SD) [38],Cu, Pb, Cd, and Zn is (0.0054; 0.0090; 0.0057; 0.0024)µg/L. Based on Table 1 shows DPAdSV-AZ method has a high enough precision because according to the Association of Official Analytical Chemist (AOAC), the value of RSD to concentrations below 1000 µg/L is smaller than 8% [39].

3.7. Application

The application of this method in the determination of Cu, Pb, Cd, and Zn metals was performed on a sample from a tap water Central Laboratory, Department of Chemistry, Andalas University used the optimum conditions of measurement obtained at accumulation potential -0.15 V, accumulation time 70s, pH 6, and AZ concentration 0.6 mmol/L. Sample measurements were made using standard addition method.

Table 2. Comparison of measurements of Cu, Pb, Cd, and Zn metals by DPAdSV-AZ method and AAS method in tap water samples

Method	Cu (µg/L)	Pb (µg/L)	Cd (µg/L)	Zn (µg/L)
DPAdSV-AZ	5.863±13	0.113±32	18.998±6	121.301±22
AAS	Not detected	Not detected	16.000±43	115.200±34

Table 2 shows the results of determination of Cu, Pb, Cd, and Zn metals with the DPAdSV-AZ method of (5.863±13); (0.113±32); (18.998±6), and (121.301±22) µg/L. The metal can be sourced from pipes used for the transportation of water from the spring to the laboratory faucet. Because the metals Cu, Pb, Cd, and Zn are used to coat the pipe for longer corrosion processes, so the water that passes through the pipe can be acidic from the process of bacterial activity and other natural activities so that over time the metal lining the pipe will be eroded.

Table 2 also shows measurements of faucet water samples using the AAS method. It aims to see the optimum accuracy of DPAdSV-AZ method that has been done. From the data shown in AAS method can detect metal Cd and Zn that is (16.000±43), and (115.200±34) µg/L. While Cu and Pb are not detected. Measurement of tap water samples by DPAdSV-AZ method was able to detect the Cu, Pb, Cd, and Zn metals simultaneously. This shows DPAdSV- AZ method is so sensitive that it can detect up to scale (µg/L to ng/L) [31-32,34].

The agreement of the compared result was tested by the paired *t*-test statistical approach [40]. Comparison *t*-test value and the critical value *(P*=0.05) for Cd and Zn metal concentrations that have been measured by DPAdSV-AZ method and AAS methods Cd obtained, The means of both analytical methods were found to be not differ significantly, since all the calculated *t*-test value were less than the critical value (2.45), the optimization of DPAdSV-AZ method shows good results.

3.8. Recovery

The accuracy level of the DPAdSV-AZ method can be seen with the determination of recovery. The identified sample concentration was added to a number of standard solutions, then compared with the sample and standard concentrations added. Determination of

recovery was studied from the tap water Central Laboratory. Department of Chemistry, Andalas University. Recovery was performed by measuring 10 mL of known concentration samples in which there was a standard solution of Cu, Pb, Cd, and Zn metals with concentrations of (5; 10, and 20) µg/L. Based on Table 3, the recovery values of each Cu, Pb, Cd, and Zn metals by DPAdSV-AZ method and set to the optimum condition studied is (98.71; 104.21; 96.60; and 99.67)%. This value indicates DPAdSV-AZ method has a fairly good accuracy because according to the Association of Official Analytical Chemist (AOAC), the value of a good recovery for the standard solution below 1000 µg/L is within the range of (70-125)% [39].

Table 3. Recovery of metals Cu, Pb, Cd, and Zn with DPAdSV-AZ method

Metal ions	Tap water Concentration (µg/L)	Added (µg /L)	Found (µg /L)	Recovery (%)	Average recovery (%)
Cu	5.863±02	5	10.334±21	95.13	98.71
	5.863±02	10	16.128±23	101.67	
	5.863±02	20	25.687±11	99.32	
Pb	0.113±23	5	5.35±25	104.69	104.21
	0.113±23	10	10.82±33	106.48	
	0.113±23	20	20.41±22	101.46	
Cd	18.998±05	5	23.68±43	98.67	96.60
	18.998±05	10	27.57±69	95.08	
	18.998±05	20	37.46±30	96.06	
Zn	121.30±11	5	126.36±27	100.05	99.67
	121.30±11	10	130.57±12	99.44	
	121.30±11	20	140.61±11	99.51	

3.9. Effects of foreign ion

Table 4 shows the effect of ion Co^{2+}, Ni^{2+}, Fe^{3+}, Cr^{6+} and K^+ against peak currents generated Cu, Pb, Cd, and Zn. Table 4 can be seen that the addition of disturbing ions did not show a significant effect on the addition of concentrations of (1and 5) mg/L, but the addition of disturbing ions at a concentration of 10 mg/L showed a significant current decrease seen in the addition of 10 mg/L ion Ni^{+2} and Co^{+2}. This can be caused because the competition between the ions Ni^{+2} and Co^{+2} form a complex with Cu, Pb, Cd, and Zn, as alizarin very effective form complex compounds with divalent metal [41-43]. Besides the half cell potential ionic Ni^{+2} and Co^{+2} located in the area of Cd and Zn metal, so that if the height of the ion concentration of Ni^{+2} and Co^{+2} will widen thereby reducing the peak current of Cd and Zn metals, but at concentrations below 10 mg/L Ni^{+2} ion peaks produced and Co^{+2} is not wide to be opportunities to do research of Cu, Pb, Cd, Co, Ni, and Zn simultaneously. The addition of 10 mg/L ion Fe^{3+} and Cr^{6+} significant decline for metals Zn, this is half-cell

potential reaction of Fe^{3+} and Cr^{6+} are potential areas that Zn metal cells at high concentrations and the lower peak will widen Zinc metal peak current [33].

KCl electrolyte can be used to support the voltammetry method [20-22] but for methods, AdSV requiring pH control are advised to use the buffer as supporting electrolyte [33]. The addition of K^+ ions at a concentration of 1 mg/L and 5 mg/L did not show a significant effect, while the addition of 10 mg/L decreased significantly peak currents on metals Cu, Pb, Cd, and Zn. It shows if using KCl as supporting electrolyte for measurement of Cu, Pb, Cd, and Zn metals should use concentration below 10 mg/L.

Table 4. Recovery of metals Cu, Pb, Cd and Zn 0.01 µg/L after addition of foreign ions

Foreign ion	concentration (mg/L)	Recovery (%)			
		Cu	**Pb**	**Cd**	**Zn**
Co^{2+}	1	99	99	99	98
	5	98	96	96	96
	10	98	95	91	94
Ni^{2+}	1	99	99	99	99
	5	98	96	94	95
	10	96	92	91	91
Fe^{3+}	1	99	99	99	99
	5	99	98	98	94
	10	97	96	96	87
Cr^{6+}	1	99	99	99	96
	5	99	98	99	93
	10	97	96	95	87
K^+	1	99	99	99	99
	5	98	98	98	96
	10	97	96	97	94

4. CONCLUSION

It can be concluded that the optimum conditions of AZ concentration 0.6 mM, pH of solution 6, accumulation potential -0.15 V and accumulation time 70 s. The RSD of metals Cu, Pb, Cd, and Zn are respectively (0.22; 0.93; 0.39, and 0.86)%. This shows that the accuracy of the method is good enough. This method was applied to the tap water samples as compared to the AAS method, Recovery of metals Cu, Pb, Cd, and Zn were (98.71; 104.21; 97.60, and 99.67)% respectively. LOD of metals Cu, Pb, Cd and Zn are (0.0054; 0.009; 0.0057, and 0.0024) µg/L. Comparison of DPAdSV-AZ method with AAS

method for metal Cd and Zn shows the calculated t-test value was less than the critical value. Recovery after the addition of ions bullies show ion Co^{2+} and Ni^{2+} 10 mg/L disruptions to metals Cd. Fe^{3+} and Cr^{6+} at a concentration of 5 mg/L and 10 mg/L indicate a problem in the Zn metal. The addition of K^+ ions showed no significant interference at a concentration of (1–5) mg/L, but at concentrations of 10 mg/L has been the disturbance in Cu, Pb, Cd, and Zn.

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