

# Simultaneous DPAdSV for Heavy Metals Determination in the Seawater of a Former Bauxite Mining Area

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## Abstract

The widespread use of HMDE for multi-ionic analysis is mainly explained by the following factors: excellent reproducibility, due to the electrode surface ease of renewal, for preventing hysteresis; wide  $E_c$ ; ability to forming amalgams with many redox-active metal ions; and (sub)nanomolar detection limits, which have unique capabilities for multi-metal determination. In this research, selectivity and sensitivity for Pb, Cd and Zn simultaneous determination, by DPAdSV, using HMDE as WE and CCA as a ligand, were tested. This method is based on the deposition of CCA-metals on Hg electrodes. The instrumental and chemical parameters that could improve measurements were obtained under optimal conditions, including: CCA concentration (0.05 mmol/L), pH (7),  $E_{dep}$  (-0.3 V)  $t_{dep}$  (60 s), AB concentration (0.5 mol/L), scan rate (150 mV/s), pulse height (80 mV), Hg drop size (4 mm<sup>2</sup>) and linearity ( $I_p$  vs concentration), which was in the range from 5 to 170, 5 to 140 and 5 to 190 M, for Pb, Cd and Zn, respectively). The LOD (S/N = 3) values were 0.05, 0.03 and 0.05 µg/L for Pb, Cd and Zn, respectively. The repeatability and intermediate precisions were tested as RSD of 0.44, 1.21 and 1.23% for Pb, Cd and Zn, respectively. The recovery values were 98, 99 and 101% for Pb, Cd and Zn, respectively. As result, the DPAdSV method with CCA ligands was successfully applied for heavy metals determination in the seawater of a former bauxite mining area.

**Keywords:** bauxite, DPAdSV, HMDE, CCA, heavy metals and voltammetry.

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## Introduction\*

The rapidly increasing water pollution is a worldwide environmental problem that threatens the life of earth inhabitants (1), and it has been caused by household and industrial waste direct and indirect disposal. Despite Pb, Cd and Zn being heavy elements that are still needed by the environment, they are non-essential metals that are considered as one of the major industrial wastewater contaminants, even at trace concentrations (2). Therefore, developing selective, sensitive, fast, simple and accurate methods is required for the determination of these metals in the environment (3-5).

Methods for the analysis of metal ions include ICP-AES (6), AAS (7), ICP-MS (8), ICP-OES (9), ISEs (10), TXRF (11) and PXRF (12). However, almost all of

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\* The abbreviations list is in pages 194-195.

these methods imply for routine operations and selection high costs, and a long time at the pre-concentration stage before measurement, for the determination of very small metal amounts (13,14). Therefore, there is the need of an alternative method that can overcome the limitations of those techniques.

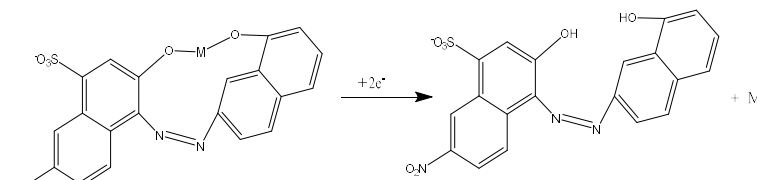
DPAdSV was chosen, because it has many advantages, such as not being affected by the seawater high salinity, having high sensitivity, low LOD, selectiveness and easy sample preparation, and being more fast and precise than of other instrument techniques (3, 15, 16). In addition, the DPAdSV preconcentration stage is shorter than that of other methods, which is generally less than one minute (17-19). DPAdSV is very sensitive, and it can be used to analyze very small concentrations ( $\mu\text{g/L}$  or  $\text{ng/L}$ ) of species in solutions (14, 20).

For heavy metals, the following voltammetric methods have previously been reported: AdSV, for Cu and Cd (21, 22); DPAdSV, for Cr (23); FSV, for Cd (24); and AdSV- RSM, for Cu (25). However, the methods are still carried out individually, which consumes a lot of time and chemical reagents, when the metals are analyzed in nature.

The voltammetric methods can simultaneously analyze several metals (4-6) (26): DPAdSV, for Pb and Zn (27); CSV, for Cu and Zn (28); SWASV, for Cd and Pb (29); ASV, for Cd and Pb (3); and CV, for Cd and Pb (19).

The results of these studies showed that the LOD was still high and the selectivity was not good enough, so, a measurement optimization was needed.

CCA functions as a ligand that can donate more than one free electron pair (hydroxyl group) to the central atom (Fig. 1), forming a complex with Pb, Cd and Zn ions (30). In this study, the DPAdSV method was used for CCA + Pb, Cd and Zn simultaneous standard setting, using a HMDE.



**Figure 1.** CCA-metals electrochemical reduction mechanism.

## Experiments

### Apparatus

DPAdSV was set by Metrohm 797 Computerce, with HMDE as the WE. The RE was Ag/AgCl/3 M KCl and the CE was Pt. A Griffin pH meter model 80, (Griffin & George Loughborough, UK), a Mettler AE 200 analytical balance (Toledo OH-USA) and glass equipment commonly used for laboratory were employed. The substances used were mother liquor Pb, Cd and Zn (1000 mg/L), KCl,  $\text{NH}_4\text{OH}$ , ammonate, acetic acid, doubly distilled water, CCA, 65%  $\text{HNO}_3$ , seawater samples, methanol and  $\text{N}_2$  gas analytical grade (Merck). The samples used came from Senggarang seawater (Tanjungpinang, Indonesia), and they were preserved with 65%  $\text{HNO}_3$ , at a ratio of 1:1000.

### Voltammetric parameters

A total of 10 mL of the sample solution was added to 0.2 mL CCA and 0.2 mL AB, and it was put into the voltammeter vessel. The solution was sterilized and purged

with  $N_2$ , for 300 s. After a new HMDE was formed, the CCA-metals adsorption was processed at current and E, for accumulated time. After resting for 10 s, DPAdSV were obtained for measuring metals CCA, with HMDE as WE.

The operating parameters of the DPAdSV-CCA method were: calibration (SAM); number of replications (3); drop size (6); stirrer speed (2000 rpm); DPAdSV mode; purge time (300 s); SR (800 mV/s); additional purge time (10 s);  $E_{ads}$  (-0.1 V);  $t_{ads}$  (70 s); equilibration time (10 s); pulse amplitude (0.05 V); start E (-0.05 V); end E (-1.3 V); voltage step (0.006 V); voltage step time (0.1 s); sweep rate (0.06 V/s); and Pb, Cd and Zn  $I_p$  values (-0.42, -0.57 and -0.99 V, respectively).

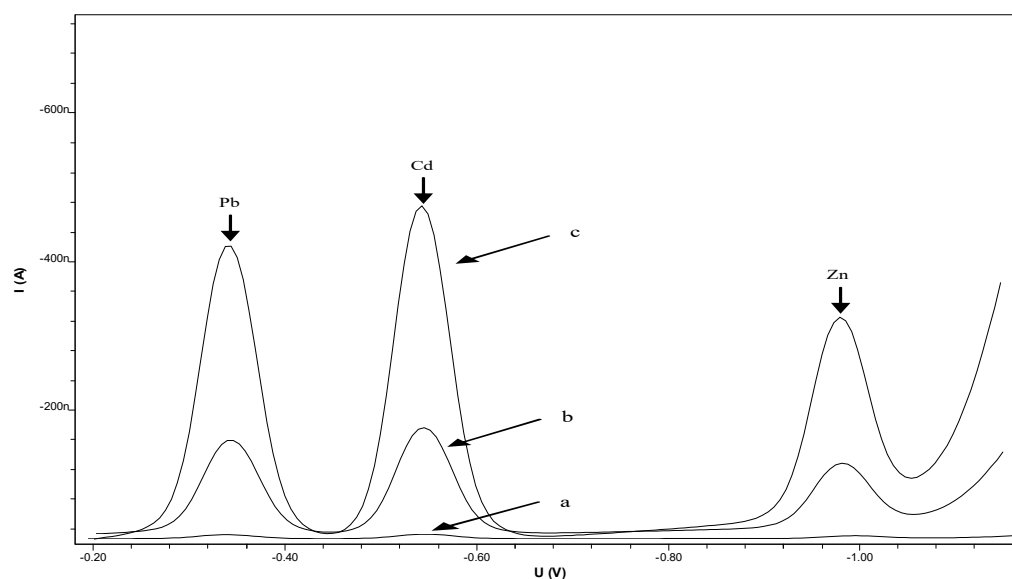
The metal ions were accumulated at the -0.1 V E on the HMDE surface. Then, they were oxidized by sweeping the potential from 0 to -1.3 V, using DPAdSV mode. Metrohm 744 pH meters were used for pH-analyte measurements, at a temperature from 25 to 30 °C. Pb, Cd, and Zn ions made the standard solution. 10 mg/L of the metal ions salts, for the DPAdSV-CCA investigations, were prepared from the stock solution of 1000 mg/L. AB and PB, with pH 2-6 and 7-8, respectively, were used as SE. 1000 mmol/L CCA stock solution were used as ligands, with all reagents of the Merck product analytical grade. Ultrapure deionization water was used for the reagents dilution, and oxygen was expelled through purging with  $N_2$  for, at least, 300 s. Whatman filter paper was used to filter samples. All experiments were carried out at room temperature.

## Result and discussion

### *Optimal conditions for DPAdSV measurements*

#### *CCA effect*

This research was conducted to optimize Pb, Cd, and Zn standard settings for DPAdSV measurement, using CCA as complexing agent. The initial experiment determined CCA suitability as a complex with metal ions, using HMDE. Fig. 2 shows the voltammograms of 0.5 mmol/L CCA (curve a), 10  $\mu$ g/L Pb, Cd and Zn ions (curve b), and 10  $\mu$ g/L Pb, Cd and Zn ions + 0.5 mmol/L CCA (curve c).

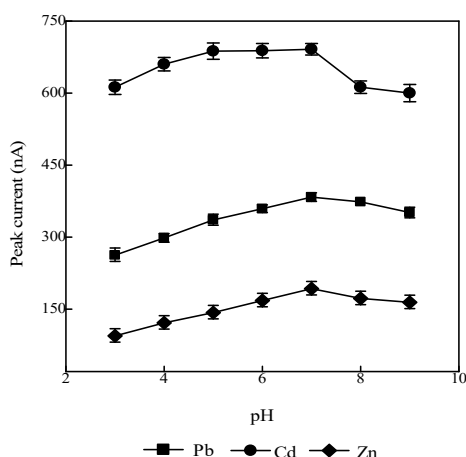


**Figure 2.** DPAdSV voltammograms of: (a) 0.5 mmol/L CCA; (b) 10  $\mu$ g/L Pb, Cd and Zn; and c) 10  $\mu$ g/L Pb, Cd and Zn + 0.5 mmol/L CCA.

Curve a shows the absence of a CCA peak in the range of Pb, Cd, and Zn ions half potential, which indicates that it did not interfere with the metal ions  $I_p$ . Curve b  $I_p$  is smaller than that of curve c. This shows that CCA can increase the reduced metal ions  $I_p$  in HMDE, which enhanced the method selectivity and sensitivity.

#### *pH variation effect*

The pH maintained the CCA-metal complex stability and produced different  $I_p$  values with each change in it. The optimized solutions pH values varied from 3 to 9 (Fig. 3).

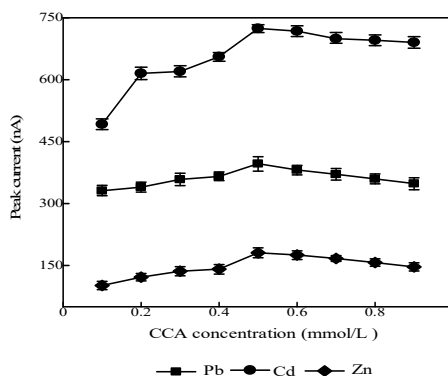


**Figure 3.** pH effect on  $I_p$ .

The solutions pH optimal determination increased the sensor selectivity, and protected the analyzed substance (CCA-metals). The solutions obtained pH (3-7) at the  $I_p$  was low, since, under acidic conditions, they contained numerous  $H^+$ , which caused the hydroxyl ( $OH^-$ ) group protonation in CCA. Hence, the CCA-metals complex that accumulated on the WE was reduced. Similarly, the obtained pH (above 7) at the  $I_p$  was low, due to the Pb, Cd, and Zn ions hydrolysis, which resulted in the disruption of the metals-CCA complex. Therefore, pH 7 was chosen for subsequent determinations.

#### *CCA concentration effect on $I_p$*

The CCA concentration range used was from 0.1 to 0.9 mmol/L (Fig. 4).

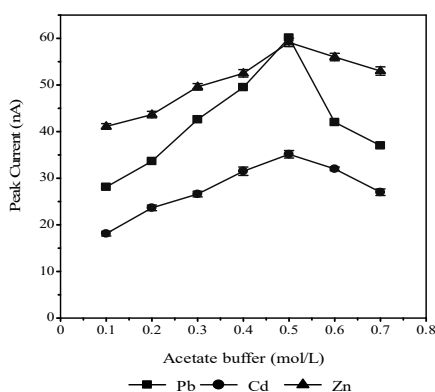


**Figure 4.** CCA concentration (mmol/L) effect on  $I_p$ .

The resulting  $I_p$  increased with higher CCA concentrations. Low CCA concentrations produced low  $I_p$ , because there was still metal ions that did not form complexes with it. At CCA concentrations above 0.6 mmol/L, the resulting  $I_p$  decreased, because only a few complexes were reduced. The results showed that 0.5 mmol/L CCA concentration was optimum, because it provided higher  $I_p$ . So, it was used in subsequent determinations.

#### SE concentration (AB) effect on $I_p$

The SE reduces the solution resistance and ions migration effect, and maintains their strength constant. The used SE was an AB, in the concentration range from 0.1 to 0.7 mol/L (Fig. 5).

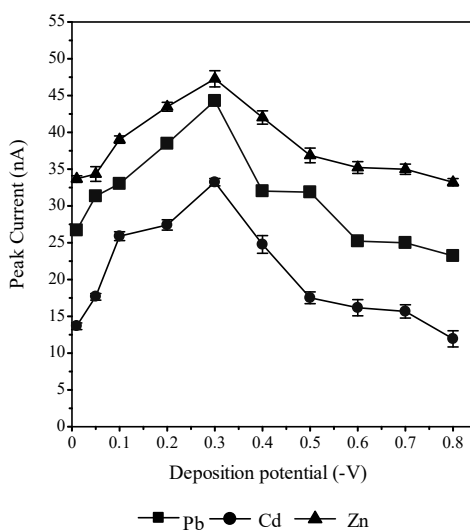


**Figure 5.** AB concentration (mol/L) effect on  $I_p$ .

The highest peak height was achieved with 0.5 mol/L AB, because the formed metals-CCA complex was the most stable and widely spread on the HMDE surface (25, 31). Therefore, 0.5 mol/L AB were used as SE in further experiments.

#### $E_{dep}$ effect on $I_p$

The Pb, Cd, and Zn ions  $E_{dep}$  effect on  $I_p$  is shown in Fig. 6.

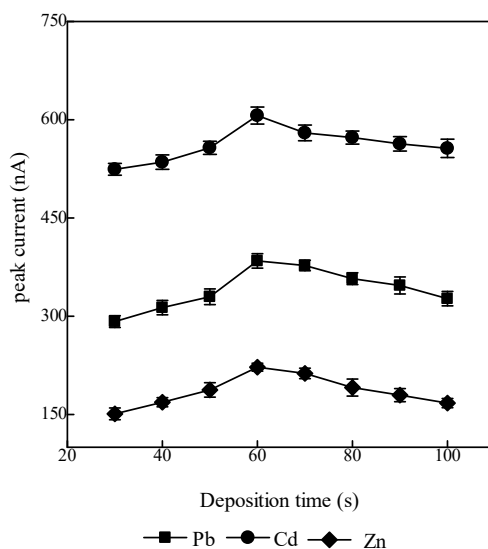


**Figure 6.**  $E_{dep}$  (-V) effect on  $I_p$ .

E was given between the WE and the RE. At the time of the reaction, the current was passed to the CE, so that the reaction that occurred on it was the opposite of the one that took place on the WE. Fig. 6 shows the effect of several  $E_{\text{dep}}$  on the generated  $I_p$ , for the optimization of E values simultaneously accumulated, from 0 to -0.8 V. At the initial measurement, the  $I_p$  increased when E went towards a negative value. However, above -0.3 V, the resulting  $I_p$  decreased, due to the perfect deposition on the electrode surface, and stripping occurrence. Therefore, when E went towards a negative value, no more analytes were deposited (3, 31). Measurement data show that the optimum  $E_{\text{dep}}$  was at -0.3 V, which was used for further determinations.

#### $T_{\text{dep}}$ effect on $I_p$

$T_{\text{dep}}$  effect of the obtained Pb, Cd, and Zn ions on  $I_p$  was studied, as shown in Fig. 7 (32).

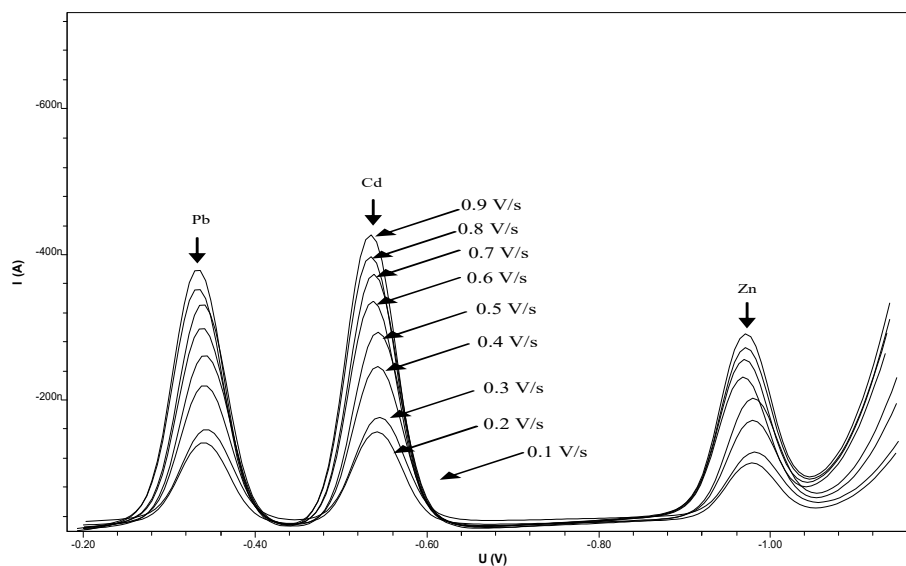


**Figure 7.**  $t_{\text{dep}}$  (s) effect on  $I_p$ .

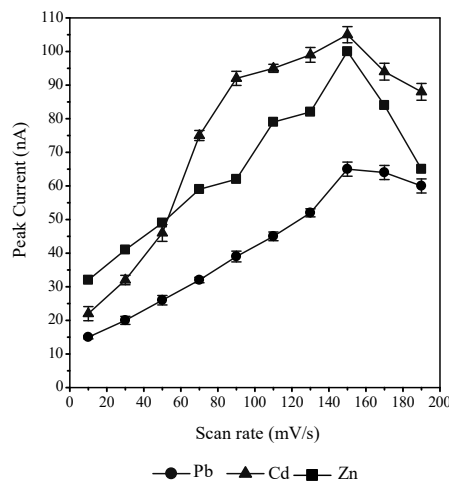
A pressure variation was obtained at 30 s, which gave a low  $I_p$ . This was due to the fact that only a small amount of the deposited analytes was adsorbed onto the electrode surface, which produced a low  $I_p$  in the stripping process. Next, a longer  $T_{\text{dep}}$  was adopted, in order to produce higher  $I_p$  values. The optimal condition was obtained from the 60 s measurement, because, during that period, the deposited analytes were more strongly adsorbed onto the electrode surface, resulting in a high  $I_p$ . The measurement was then carried out at the  $T_{\text{dep}}$  of 70 s, which apparently resulted in a lower  $I_p$  than that obtained with 60 s, due to the electrode surface saturation, so that not all analytes were released from it, during the stripping process. So, a  $t_{\text{dep}}$  of 60 s was used in further determinations.

#### Effect of DPAdSV parameters on pulse amplitude and SR

This study has tried to increase the sensitivity of the metals-CCA determination and test the influence of DPAdSV parameters on pulse amplitude (Fig. 8) and SR (Fig. 9).



**Figure 8.** Pb, Cd and Zn DPAdSV effect on pulse amplitude (V/s).



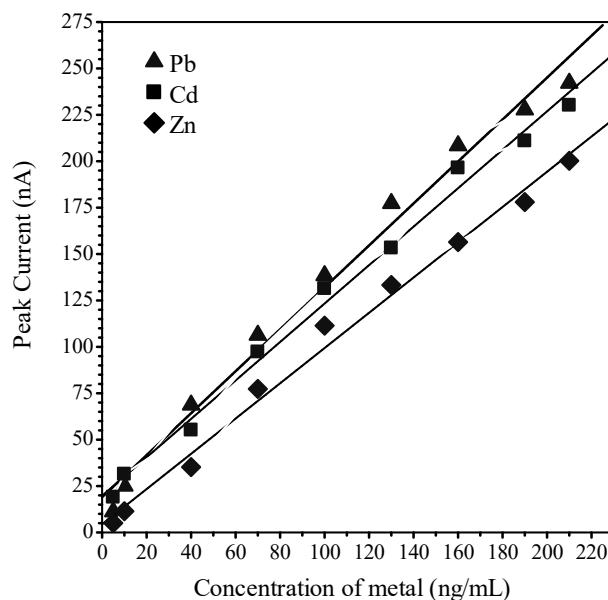
**Figure 9.** Scan rate (mV/s) effect on  $I_p$ .

The obtained pulse amplitude and SR ranged from 0.1 to 0.9 V/s and from 10 to 190 mV/s, respectively. The higher the metals  $I_p$ , the more widened were Pb, Cd and Zn voltammograms. This caused an overlap in the voltammograms and a decrease in the metals  $I_p$  (13). Therefore, the pulse amplitude of 0.8 V/s and the SR of 150 mV/s were selected. HMD size was from 0.25 to 4 mm<sup>2</sup>. The greater the HMD drop size, the higher the metals  $I_p$ , but if it was too high, it would fall before the metals reduction process took place (33). Metals-CCA  $I_p$  increased with higher frequency values, from 10 to 100 Hz. The 25 Hz frequency was chosen as the optimum condition, because it showed a voltammogram shape that was symmetrical and did not widen.

### **Analytical parameters**

Linearity ( $I_p$  vs concentration) was in the range from 5 to 170, 5 to 140 and 5 to 190 M, for Pb, Cd and Zn, respectively (Fig. 10). The obtained  $R^2$  values were 0.9867, 0.9987 and 0.99865, for Pb, Cd and Zn, respectively. LOD was calculated

by  $3 \times SD/m$ , which is the calibration curve slope obtained at 0.05, 0.03 and 0.05  $\mu\text{g/L}$ , for Cd, Pb and Zn, respectively. The analytical method accuracy determination was calculated from the measurement of 10 replications, with 10  $\mu\text{g/L}$  Pb, Cd and Zn. The obtained RSD was 0.44, 1.21 and 1.23%, for Pb, Cd and Zn, respectively. The determination accuracy was calculated by the seawater samples recovery values, which were 98, 99 and 101%, for Pb, Cd and Zn, respectively.



**Figure 10.** DPAdSV of the solutions with different concentrations.

RSD and recovery values were good. According to AOAC, the standard method for metals with a concentration of 10  $\mu\text{g/L}$  gives RSD values below 15%, and the recovery values range from 75 to 115%. Based on the obtained data, this method can be used, because it has lower values than the recommended threshold, and it has high accuracy (34). Table 1 shows that the DPAdSV-CCA method has sensitivity and selectivity, compared to the potentiometric technique using ISE, for Pb, Cd and Zn determination.

**Table 1.** Comparison of recovery and LOD values of the DPAdSV-CCA method with those of the potentiometric technique using ISE.

Method	Recovery(%)			LOD ( $\mu\text{g/L}$ )			Ref.
	Pb	Cd	Zn	Pb	Cd	Zn	
ISE membrane	90.8			3.31			(35)
Multiple ISE array			86			4.6	(36)
C/PANI-TiO <sub>2</sub> /Pb <sup>2+</sup> -ISE				2.2			(37)
ISE-K-polypyrro						11.2	(38)
ANTI-DMN-ISE						2.01	(39)
Salen material-ISE		104			3.2		(40)
DPASV-Activated <i>Hordeum vulgare</i>	96	97		6.96	1.82		(41)
SWASV-ISE	90	122		0.7	0.41		(42)
BiSn film GCE	102	82	90	0.4	0.6	0.5	(43)
PEDOT-PF <sub>3</sub>	97			0.166			(44)
DPAdSV-CCA	98	99	101	0.05	0.03	0.05	This study

salen material: (bis(salicylaldehydo)ethylenediimine)



### Cationic and anionic interferences

Possible cationic and anionic interference on Pb, Cd and Zn simultaneous measurements, using the DPAdSV method, with CCA as the determined complex compounder, were tested. The measurements were made on 10 µg/L Pb, Cd and Zn, using the optimum conditions that had been obtained for each of them. The tested cationic and anionic concentrations were from 1 to 10 mg/L Cu<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Sr<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, Al<sup>3+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, Br<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, SCN<sup>-</sup> and NO<sub>3</sub><sup>-</sup> (Table 2).

**Table 2.** 10 µg/L Pb, Cd and Zn percentage recovery after the interfering ions addition.

Interferent	Concentration (mg/L)	Signal recovery rate (%)		
		Pb	Cd	Zn
Cu <sup>2+</sup>	10	97.7	99.2	99.5
Ca <sup>2+</sup>	10	98.1	97.4	99.3
Ni <sup>2+</sup>	10	98.4	98.4	98.6
Co <sup>2+</sup>	10	97.8	97.9	98.7
Fe <sup>3+</sup>	10	99.1	98.5	98.7
Sr <sup>2+</sup>	10	98.6	98.2	98.9
K <sup>+</sup>	10	98.3	99.1	99.2
Na <sup>+</sup>	10	98.7	98.9	99.2
Li <sup>+</sup>	10	99.1	99.4	99.6
Al <sup>3+</sup>	10	98.9	98.2	99.5
Mn <sup>2+</sup>	10	97.9	97.9	98.9
Mg <sup>2+</sup>	10	98.6	99.2	99.4
NH <sub>4</sub> <sup>+</sup>	10	99.7	99.8	99.4
Cl <sup>-</sup>	10	99.1	98.7	98.5
CO <sub>3</sub> <sup>2-</sup>	10	97.8	99.1	98.9
SO <sub>4</sub> <sup>2-</sup>	10	98.9	98.3	99.3
Br <sup>-</sup>	10	99.3	97.9	98.4
ClO <sub>4</sub> <sup>-</sup>	10	99.5	98.5	98.7
SCN <sup>-</sup>	10	98.6	98.8	98.4
NO <sub>3</sub> <sup>-</sup>	10	99.1	98.2	99.3

The test results showed no disturbance in Pb, Cd, and Zn measurements up to the concentration of 10 mg/L, revealing that they were cationic and ionic. This shows that the DPAdSV-CCA method for Pb, Cd, and Zn simultaneous determination has good selectivity.

### Application on real samples

The proposed DPAdSV-CCA method was applied to the seawater of former bauxite mining area samples. SAM was used as sample determination to eliminate matrix effects. Pb and Cd highest concentrations found in seawater were 15.34 ± 1.5 and 9.22 ± 0.4 µg/L, respectively (Table 3).

**Table 3.** DPAdSV-CCA Pb, Cd, and Zn determination in the seawater of a former bauxite mining area.

Sample	Metals		
	Pb (µg/L)	Cd (µg/L)	Zn (µg/L)
Seawater I	15.34±1.5	9.22±0.4	35.11±0.5
Seawater II	9.11±0.2	5.16±1.9	19.21±4.1
Seawater III	4.76±1.6	7.76±3.1	15.76±0.9

Based on Pb, Cd and Zn minimum concentrations, the obtained seawater was still below the recommendations of US-EPA (45). The ability of DPAdSV-CCA for Pb, Cd, and Zn simultaneous determination, in natural samples with very low concentrations ( $\mu\text{g/L}$ ), indicates that this method is very sensitive and does not affect the measurement of seawater samples that have a very large matrix.

### Conclusion

The DPAdSV method for the simultaneous determination of Pb, Cd, and Zn-CAC complex tracing concentrations on its deposition was successfully used in the seawater of former bauxite mining area samples. This method has high sensitivity, good selectivity and low costs, and worked quickly with the obtained optimum conditions: CCA concentration (0.05 mmol/L), pH 7,  $E_{\text{dep}}$  (-0.3 V),  $t_{\text{dep}}$  (60 s), AB concentration (0.5 mol/L), SR (150 mV/s,) pulse height (80 Mv), HMD size (4 mm<sup>2</sup>) and linearity ( $I_p$  vs. concentration), which was in the range from 5 to 170, 5 to 140 and 5 to 190 M, for Pb, Cd and Zn, respectively.

The LOD values were 0.05, 0.03 and 0.05  $\mu\text{g/L}$  for Pb, Cd and Zn, respectively. The RSD was 0.44, 1.21 and 1.23%, for Pb, Cd and Zn, respectively. The recovery values were 98, 99 and 101%, for Pb, Cd and Zn, respectively.

The addition of 1-10 mg/L cationic and anionic concentrations showed no significant disturbance to the simultaneous measurement of 10 g/L Pb, Cd and Zn, using the DPAdSV-CCA method. This shows that DPAdSV-CCA has good selectivity and sensitivity. It was applied for the simultaneous measurement of Pb, Cd and Zn concentrations from 4 to 15, 5 to 9 and 15 to 35 g/L, respectively, in the seawater of former bauxite mines.

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### Authors' contribution

**H. Pardi:** conceived and designed the analysis; collected the data; wrote the paper. **D. Fitriyah:** collected the data; contributed with data or analysis tools. **F. S. Silitonga:** conceived and designed the analysis; contributed with data or analysis tools. **T.W. Edelwis:** conceived and designed the analysis; collected the data; wrote the paper. **E. P. Ramdhani:** collected the data; contributed with data or analysis tools; performed the analysis.

### Abbreviations

**AAS:** atomic absorption spectrometry

**AB:** acetate buffer

**AdSV:** adsorptive stripping voltammetry

**ANTI-DMN:** 4-antipyrene carboxaldehyde and diaminomaleonitrile Schiff based probe

**AOAC:** Association of Official Agricultural Chemists

**ASV:** anodic stripping voltammetry

**CCA:** calconcarboxylic acid

**CE:** counter electrode  
**CSV:** cathodic stripping voltammetry  
**CV:** cyclic voltammetry  
**DPAdSV:** differential pulse adsorptive stripping voltammetry  
**E<sub>ads</sub>:** potential of adsorption  
**E<sub>c</sub>:** cathodic potential  
**E<sub>dep</sub>:** deposition potential  
**FSV:** fast scan voltammetry  
**GCE:** glassy carbon electrodes  
**HMDE:** hanging mercury drop electrode  
**HNO<sub>3</sub>:** nitric acid  
**i<sub>c</sub>:** cathodic current  
**ICP-AES:** inductively coupled plasma atomic emission spectroscopy  
**ICP-MS:** inductively coupled plasma-mass spectrometry  
**ICP-OES:** inductively coupled plasma optical emission spectrophotometry  
**I<sub>p</sub>:** peak current  
**ISE:** ion-selective electrodes  
**LOD:** limit of detection  
**NH<sub>4</sub>OH:** ammonium hydroxide  
**PANI-TiO<sub>2</sub>:** polyaniline-doped titanium dioxide  
**PB:** phosphate buffers  
**PEDOT-PF<sub>3</sub>:** micro/nano porous 3D poly(3,4-ethyl-enedioxythiophene)/K<sub>3</sub>Fe(CN)<sub>6</sub>  
**PXRF:** portable X-ray fluorescence  
**RE:** reference electrode  
**RSD:** relative standard deviation  
**RSM:** response surface methodology  
**SAM:** standard addition method  
**SD:** standard deviation  
**SD/m:** standard deviation/slope  
**SE:** supporting electrolyte  
**S/N:** signal to noise ratio  
**SR:** scan rate  
**SWASV:** square-wave anodic stripping voltammetry  
**t<sub>ads</sub>:** time of adsorption  
**t<sub>dep</sub>:** deposition time  
**TXRF:** total reflection X-Ray fluorescence spectroscopy  
**US-EPA:** United States Environmental Protection Agency  
**WE:** working electrode

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