

The development of differential pulse anodic stripping voltammetry method to determine of ziram (fungicide ditiocarbamat) with Hanging Mercury Drop Electrode (HMDE)

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Abstract

A differential pulse anodic stripping voltammetric technique has been used previously for the determination of the pesticide, ziram, in rice samples using a static mercury drop electrode. Based on Mathew's research, differential pulse anodic stripping voltammetric was developed to distinguish inorganic zinc and ziram zinc in sodium acetate-sodium chloride media using a hanging mercury drop electrode (HMDE). The determination of ziram using the HMDE was studied in various conditions of : supporting electrolytes, deposition potential, deposition time, scan rate and modulation amplitude. The result of the study indicated that zinc chloride (inorganic zinc) and ziram zinc could be differentiated as they give well-resolved peaks at -1.16 V and -1.00 V vs Ag/AgCl(KCl 3M) electrode in sodium acetate- sodium chloride media. The stripping signal attained a maximum at a deposisiion potential of -1.3 V for 300 seconds and anodically scan the potential from -1.4 V to -0.8 V with a scan rate of 2 mV/s and a modulation amplitude of 25 mV. The analytical performance characteristics of the probe indicated : precision 0.1 - 1.4 %, sensitivity 1µg/L/nA and the calibration plot is linear up to 305 µg/L.

Keywords: Ziram, zinc, anodic stripping voltammetry

Introduction

Residu of pesticides found in agriculture product, drinking water, and anvironmental exposure has raised much concern from the general public in recent years. Thousands of pepticides of various types – insecticides, bactericides, fungicides, herbicides, rodenticides or fumigants are used in large quantity annually. The major purpose of designing these chemicals intends for destroying pests and improving productivity. However, residuals of these compounds in the foodstuffs or in the environments also lead to a serious threat to public health.

Ziram or cumin L is the common name for zinc dimethyldithiocarbamate which is used as an agricultural fungicide because of its low phytotoxicity and is applied in the rubber industry as a vulcanization accelerator and antioxidant. Commond methods of determination of ziram are spectrophotometry, head space GC and HPLC. Mathew reported a differential pulse anodic stripping voltammetric determination of ziram using a static mercury drop electrode. This procedure developed distinguishes inorganic zinc and ziram zinc in sodium acetate-sodium chloride media.

This research is going to consider to employ the electrode of hanging mercury drop electrode (HMDE) on the determination of ziram with differential pulse anodic stripping voltammetry by supporting electrode Ag/AgCl (KCl 3M) in the medium of natrium acetate – natrium chloride.

Materials and Methods

Apparatus

Stripping voltammograms were recorded with METROHM Model C757 with hanging mercury drop electrode (HMDE). Deaeration was done with purified nitrogen. The reference electrode was Ag/AgCl with an auxillary Pt electrode.

Reagents

Ziram stock solution 10^{-3} M was prepared by dissolving 0.0762 g ziram in hot 2 N HCl and making up with bidistilled water to 250 mL. Sodium acetate (1.0 M) and sodium chloride (1.0 M) were prepared in bidistilled water.

Procedure

Transfer a suitable aliquout of sample solution containing 0.1 – 6 µg ziram (up to 8 mL) into a 10 mL calibrated flask. Add 1 mL of sodium acetate and 1 mL of sodium chloride, dilute to volume with bidistilled water, transfer the solution into the electrochemical cell and place the HMDE in it. After deaeration, deposit for 4 min at -1.4V vs. Ag/AgCl with stirring, switch off the stirrer, allow 30 s for the turbulence to cease and anodically scan the potential from -1.4 to -0.8 V with a scan rate of 2 mVs⁻¹ and a pulse amplitude of 25 mV. Construct a calibration

graph for various concentrations of ziram by plotting peak current vs. concentration of ziram.

Results and Discussion

These studies revealed that ziram zinc gives a stripping peak at 1.00 V after deposition at -1.4 V for 4 min (curve B, Fig.1). In contrast, for inorganic zinc the stripping peak occurs at -1.16 V under identical conditions (curve A, Fig 1). This indicates that DPASV with HMDE studies can distinguish ziram zinc and inorganic zinc in sodium acetate-NaCl medium. Detailed optimization studies for the determination of ziram were conducted and the results obtained are describe below.

Effect of supporting electrolyte

The determination of 5×10^{-7} M ziram using the HMDE with deposition for 4 min at -1.4 V was studied in different supporting electrolytes. The results are shown in tble 1, from which it is clear that the acetate-chloride medium gives the maximum stripping current signal compared to acetate or NaCl. Furthtermore, the stripping peaks of ziram zinc and inorganic zinc are resolved in NaCl or acetate-chloride.

Table 1 Stripping current obtained for ziram in various supportingelectrolytes after deposition at -1.4 V vs Ag/AgCl for 240 second, scan rate 2mVs^{-1} and pH 5

Supporting electrolyte	$I_p(\text{nA})$
HCl (0.1M)	
Ammonium acetate (0.1M)	0.5
Sodium chloride (0.1M)	32.0
Sodium acetate (0.1M)	21.0
Sodium acetate (0.1M) + NaCl (0,1 M)	24.8
	53.0

Variation of deposition potential

The preconcentration potential also is a major factor affecting the response sensitivity. In order to ascertain the optimum deposition the optimum deposition potential the cathodic limit of the deposition potential was varied in the range -1.2 V to -1.6 V vs. Ag/AgCl with deposition for 4 min at each deposition potential, followed by a DPASV scan rate of 2mVs^{-1} and a modulation amplitude 25 mV. The magnitude of the stripping signal attains a maximum at a deposition potential of -1.3 V vs. Ag/AgCl. The sensitivity decreases sharply at potential less than -1.3 V and only limited sensitivity is observed -1.0 V.

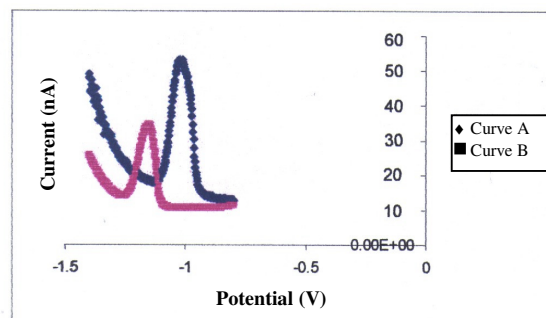


Figure 1 Differential pulse anodic stripping voltammograms recorded for 10^{-7} M inorganic zinc and ziram zinc after deposition at -1.4 V vs Ag/AgCl for 240 second, pH 5 (0,1 M sodium acetate + 0.1 M sodium chloride, scan rate 2mVs^{-1})

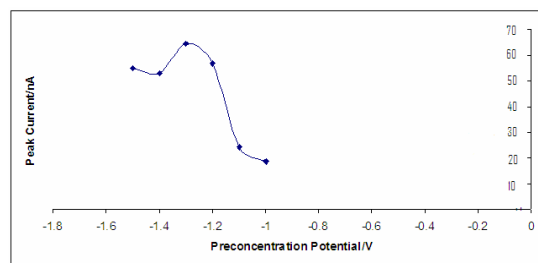


Figure 2 Effect of preconcentration potential study on the differential pulse stripping voltammograms

Variation of deposition time

The effect of deposition time (120 – 360 s) on the magnitude of the stripping signal was studied. The stripping signal varied liniarly with the deposition time and a deposition time of 240 s was chosen to offer reasonable sensitivity.

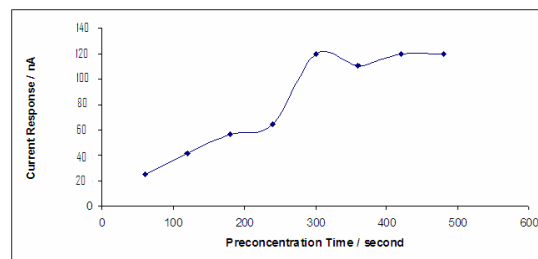


Figure 3 Effect of preconcentration time study for 5×10^{-7} M ziram using the HMDE

Variation of scan rate

The effect of scan rate in the range $1 - 5\text{mVs}^{-1}$ was studied during DPASV determination of ziram. At 2

mVs^{-1} the sensitivity and resolution of the ziram zinc and inorganic zinc were found to be optimum.

Variation of modulation amplitude

The modulation amplitude was varied from 15 – 35 mV during DPASV determination of ziram. At 25 mV the resolution of ziram zinc and inorganic zinc was optimum and reasonably sensitive.

Conclusions

Finally, from the result can be taken the conclusion below:

1. The anorganic and ziram of zincs can be separated by differential pulse anodic stripping voltammetry with working electrode of hanging mercury drop electrode (HMDE).
2. The optimum condition of ziram's measurement by differential pulse anodic stripping voltammetry with the working electrode of HMDE is as following: at potential of deposition is -1.3 V against the supporting of standard of comparison of electrode Ag/AgCl (KCl 3M) and time of deposition is 300 seconds, the scanning speed is 2

mV/s and the amplitude of modulation is 25 mV then the early of measurement is -1.4 V and the end is -0.8 V.

3. The performance of analyses procedure showed the range of fix curve linearity until 305 $\mu\text{g/L}$ of ziram, sensitivity 1 $\mu\text{g/L/nA}$, accurate 0.1 – 1.4%, and precision 1.1% - 7.3% .

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