

Adsorptive Stripping Voltammetric Determination of the Pesticide Chinomethionate in Fruits

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The electrochemical behaviour of the pesticide chinomethionate at a hanging mercury drop electrode is investigated. Differential pulse stripping voltammetry was used to determine chinomethionate in the presence of Britton-Robison (B-R) medium pH 4.56. Different parameters were tested to optimize the conditions for the determination of chinomethionate. The adsorbed form is reduced irreversibly. The linear concentration range is from 0.5-8.0 ng mL⁻¹ chinomethionate. In this method, chinomethionate of 0.5 ng mL⁻¹ with accumulation time 150 s can be determined successfully. This method was applied to analyze the spiked samples of apples and pears and found recoveries and relative standard deviation in the range of 89.33-98.00 % and 2.8-4.5 %, respectively.

Key Words: Differential pulse stripping voltammetry, Chinomethionate, Fruit, Pesticide.

INTRODUCTION

Now-a-days a number of pesticides are commercially available in thousands of market names for using as insecticides, bactericides, fungicides, herbicides, rodenticides or fumigants. The major purpose of designing these chemicals intends for destroying pests and improving productivity. However, residues of these compounds in the foodstuffs or in the environments also lead to a serious threat to public health. Chinomethionate (6-methyl-2,3-quinoxalinedithiol cyclic carbonate) (CM), which is used as an acaricide as well as a fungicide, showed high toxicity to many species. One of the structural distinctiveness of this fungicide is the possession of 1,3-dithio-2-one as its reactive functionality. It was reported in the past that the field workers using chinomethionate have experienced severe skin irradiation when they were exposed to sunlight¹. In addition, it was found that the half-life of this fungicide on apple leaves in the sun was much shorter than those in the shady areas. It is also effective against pear psylla, white flies and aphids and has given excellent control of powdery mildew on a variety of crops. In the South Africa the maximum residue level (MRL) of CM permitted in apples, is 0.2 mg kg⁻¹².

Differential pulse stripping voltammetry is a technique in which the analyte is preconcentrated first by adsorption onto a working electrode surface followed by the voltammetric reduction of the electroactive species. Furthermore, stripping voltammetry is an important technique for trace determination of many inorganic and organic substances³. The stripping technique has been used successfully for the determination of

subnanogram level of several pesticides^{4,5}. This technique is less time-consuming, eliminates cumbersome solvent extraction and cleanup steps and avoid calculations for recovery that are commonly practiced to photometric and chromatographic methods while the resulting accuracy and precision are at least comparable.

In our previous work, application of electrochemical methods in organic pesticide residues analysis was reviewed⁶. Carbamate pesticides⁷ and organophosphorus pesticides⁸ were analyzed successfully by voltammetry method. The aim of this work was to optimize and characterize an effective adsorptive-stripping voltammetric protocol for trace measurements of CM at hanging mercury drop electrode (HMDE), based on the adsorptive accumulation of CM. Chromatographic techniques are widely employed since they are powerful separation techniques. Although spectrofluorimetry method^{9,10} is used for this determination in water and vegetable samples, this pesticide is commonly determined by gas chromatography method with mass spectrometric detection¹¹⁻¹³, sometimes in combination with the quick easy cheap effective rugged and safe (QuEChERS) sample preparation method¹⁴, solid-phase microextraction¹⁵ and supercritical fluid extraction¹⁶. Comparing with GC, the advantages of the electrochemical methods are mainly contributed to their convenience, easy sample preparation, high sensitivity and sometimes high selectivity¹⁷. However, there are no early reports on the voltammetric determination of CM. As will be illustrated below, the adsorptive accumulation of CM onto the HMDE results in a highly sensitive and reproducible DPSV protocol for measuring trace levels of CM.

EXPERIMENTAL

The voltammetric measurements were carried out employing the Electrochemical Analyzers models 263A and 394-PAR (Princeton Applied Research PAR, Princeton, NJ, USA). The electrode assembly (303A-PAR) incorporated with a micro-electrolysis cell comprising of a hanging mercury drop electrode (HMDE) as a working electrode, an Ag/AgCl/KCl 3 M reference electrode and a platinum wire auxiliary electrode, was used for all the electrochemical techniques.

A stock solution of 100 mg L⁻¹ CM (Aldrich Chemical Company, Inc.) was prepared by dissolution of the appropriate amount of CM in absolute ethanol. Fresh solutions of lower concentrations were prepared by appropriate dilution of the stock solution with absolute ethanol. Britton-Robinson buffer of pH 2-11 (a mixture of an equal volumes of 0.04 mol L⁻¹ of boric, acetic and phosphoric acids, the pH was adjusted by 0.2 mol L⁻¹ sodium hydroxide solution) was prepared in distilled water. The supporting solutions were prepared from the analytical-reagent grade chemicals: citrate, disodium hydrogen phosphate, trisodium phosphate. All the solvents (acetone, ethanol and hexane) were of HPLC grade. Anhydrous sodium sulfate (dried at 650 °C for 4 h and stored in a desiccator) was of analytical grade. Analytical reagent grade chemicals and distilled water were used unless otherwise specified.

General procedure: A suitable amount of the CM, together with 2 mL pH 4.56 Britton-Robinson buffer solution, was transferred to an electrochemical cell and diluted to 10 mL with distilled water. After deaeration with nitrogen for 6 min, the analytes were pre-concentrated at -300 mV for 150 s. When the accumulation time was completed, the stirring was stopped and, after a 10 s static period, a differential pulse voltammetric scan, with a scan rate of 20 mV s⁻¹ and a 50 mV pulse amplitude was run from -550 to -800 mV at a hanging mercury drop (small size).

Commercial sample preparation: A fresh commercial fruit sample (mean weight 200 g) was chopped and homogenized with a mixer. The sample was then spiked with an addition of suitable amount CM (the content of CM was matched 5, 10 and 20 µg kg⁻¹ for apple and 7.5, 15 and 25 µg kg⁻¹ for pear in the original sample). 400 mL of acetone was added and was blended at high speed for 3 min. The mixture was made to 600 mL with acetone and blend for an additional 2 min. Because CM is relatively nonpolar, it can be quantitatively extracted from a 2:1 acetone:water solution into an equal volume of hexane¹⁸. After filtration, exactly 300 mL of extract was transferred to a 1 L separatory funnel and extracted with 300 mL of hexane. The filtrate was through a 250 g bed of anhydrous Na₂SO₄ and rinsed with an additional 50 mL of hexane. The sample was evaporated to 100 mL and was filtered again, with rinsing twice with 25 mL hexane. The combined filtrate was evaporated just to dryness. The residue of CM was dissolved in ethanol and transferred to a 50 mL volumetric flask.

RESULTS AND DISCUSSION

Cyclic voltammetry: Fig. 1 shows three cyclic voltammograms of 8 ng mL⁻¹ CM in B-R buffers of pH 4.56 at accumulation potential -300 mV, preconcentration time 60 s

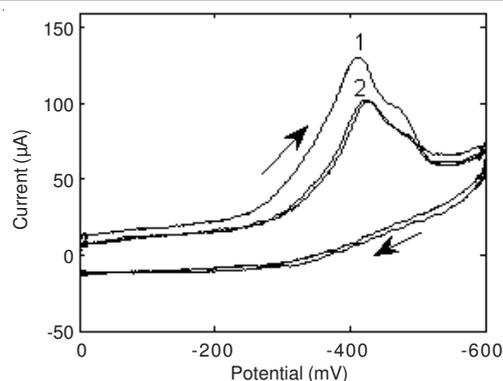


Fig. 1. Cyclic voltammograms of 8 ng mL⁻¹ CM in a B-R buffer

and scan rate 20 mV s⁻¹. The cathodic reduction peak is located at -0.655 V and there is not current signal in the reverse direction, within the potential range selected. A much developed peak current intensity was achieved following accumulation of CM onto the HMDE surface whereas its second cycle at the same mercury drop exhibited a lower peak current intensity. This behaviour indicated the interfacial adsorptive character of CM onto the mercury electrode surface. The adsorption effect was also identified by a plot of log *i*_p versus log *v* giving a straight line which can be expressed by the equation: log *i*_p (µA) = -72.32 + 0.913 log *v* (V s⁻¹). A slope close to 1.0 shows that the compound was adsorbed on the electrode surface.

Effect of supporting electrolyte and pH: A series of supporting electrolytes (0.04 mol L⁻¹ citrate, 0.05 mol L⁻¹ disodium hydrogen phosphate, trisodium phosphate and 0.04 mol L⁻¹ B-R buffer) were tested in the presence of 4 ng mL⁻¹ CM and 150 s accumulation time. Both the peak height and the peak shape were taken in consideration during choosing the supporting electrolyte. The results showed that B-R buffer gave the best background and signal response. Generally speaking, the higher the supporting electrolyte concentrations are, the higher the peak currents are. In this work, the concentration of B-R buffer solution increases significantly, but the peak current increases slightly. Considering the peak sensitivity and chemical reagent saving, a B-R buffer of 0.008 mol L⁻¹ was selected. The solution condition such as the pH and the concentration of CM, affect the peak potential and peak current significantly. The effect of pH was investigated. A larger current was observed at pH < 9.0, which decreases gradually up to pH 10.38. At higher pH, the decrease in current and broadening of the peak were observed. The peak potential is also shifted to more negative values with increasing pH (Fig. 2). This behaviour indicates that hydrogen ion is participating in the electrode process. Taking into account these results, the medium chosen to carry out further studies was the Britton-Robinson buffer solution at pH 4.56.

Reduction mechanism for the chinomethionate: The peak potential and pH was linear, which well fitted the equation: *E*_p (mV) = 81.2 pH + 463 (r = 0.973). According to the Nernst equation: *E*_p = *E*^o - 2.303 (RT/*m*nF) pH (where *m* is the number of hydrogen ions involved in the reaction), the value of *m* can be calculated. On the other hand, the half peak width equation for an irreversible electrochemical reaction is *w*_{1/2} = 62.4/*αn*¹⁹ where *α* is the transfer coefficient and *n* is the number of

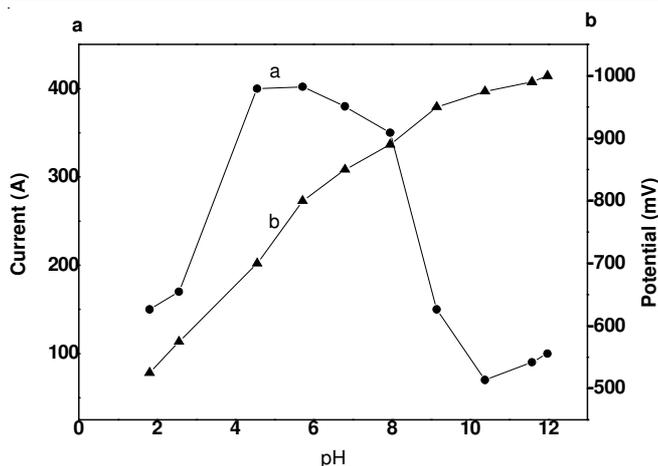


Fig. 2. Effect of pH on the differential pulse stripping peak current, a and peak potential, b of (4.0 ng mL⁻¹ CM) in B-R buffer solution at accumulation potential -300 mV, preconcentration time 150 s, scan rate 20 mV s⁻¹ and pulse amplitude 50 mV

electrons transferred. From the cyclic voltammogram, the $\omega_{1/2}$ was estimated to be 53, which was substituted into the above equation to give a value of 1.18 for αn . In general, α is taken as 0.5 for an irreversible reaction and thus by comparison the number of electrons transferred in the electrode is equal to 2. So a value of 1.62 for m can be calculated from the slope of the plot of E_p versus pH. Therefore, it can be concluded that two hydrogen ions are involved in the electrode reaction.

Effect of accumulation potential and scan rate: The effect of the potential on the stripping peak current was examined over the range +0.2 to -0.5 V by differential pulse stripping voltammetry. The results showed that the peak height decreases with the positive direction from -0.5 to +0.2 V. -0.3 V was chosen to avoid the bad-defined peak at more negative potential. Stripping voltammetry was also carried for increasing values of the scan rate (v) under the above optimized conditions. They gave rise to reduction peaks with intensities that showed a linear increase with the scan rate between 10-200 mV s⁻¹, according to the following relationship: I_p (nA) = 1.23 (v/V s⁻¹) + 0.32 ($r = 0.997$), where r is the correlation coefficient. It was found that the peak current increases and the peak potential shifts to more negative values with increasing scan rate. The plot of peak current against scan rate (v) gave a straight line with a slope of 1.23. A slope of 1.0 is expected for ideal reaction of surface species²⁰.

Effect of preconcentration time: Fig. 3 shows the effect of preconcentration time in the presence of different concentrations of CM by differential pulse stripping voltammetry. The peak current increased linearly with preconcentration time up to 450 s. A deviation from the linearity was observed at accumulation times longer than 330 s for both 1 and 5 ng mL⁻¹ CM, respectively, which indicate the mercury drop saturation. A preconcentration time of 150 s was adopted in the present study for the stripping analysis of CM. It is because that the sensitivity for 150 s is enough for the residue determination and some fouled adsorption might be avoided.

Effect of other parameters: Other experimental parameters such as temperature and ionic strength were optimized. The dependence of peak currents on CM concentration at different temperature (10-60 °C) was studied. The peak current

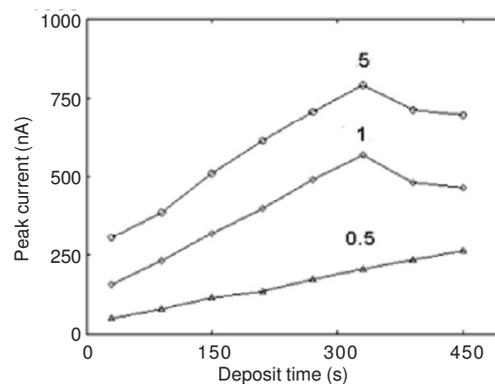


Fig. 3. Plot of current against current in presence of B-R buffer solution (pH 4.56) for different CM solutions by differential pulse stripping voltammetry and the unit is ng mL⁻¹

decreases as temperature increases for a given CM concentration, indicating low temperature improve the adsorption of CM on electrode. The value chosen was 20 °C because it was room temperature. Ionic strength for 0.01, 0.05 and 0.1 mol L⁻¹ was adjusted by adding suitable amount of KCl solution in the electrochemical cell. Although when the ionic strength increases the stripping peak current decreases, no ionic strength adjustment was used because the ionic strength conditions were already imposed by the buffer solution needed to raise the optimized 4.56 pH value.

Several instrumental parameters which directly affect the voltammetric response were optimized, *i.e.*, drop size, scan rate and pulse amplitude. The working conditions decided upon were: small size, 20 mV s⁻¹ and 50 mV.

The stripping currents were not modified when varying the rest period, since it was found the 10s was sufficient to allow for the formation of a uniform concentration of the analyte in the mercury drop.

Calibration plot: Differential pulse stripping voltammetry was applied to the quantitation of CM in the optimal condition and yielded well-defined peaks versus Ag/AgCl reference electrode. It was also found that all the peak currents increased linearly with their increasing amounts at different accumulation time (90, 150 and 300 s). The linear calibration parameters were then calculated²¹ and the statistical characteristics are summarized in Table-1. The detection limit obtained is 0.12 ng mL⁻¹ at the accumulation time 150 s. The precision was good; the relative standard deviation of ten determinations at 2 ng mL⁻¹ level was 2.2 % after 150 s accumulation time. It was found that the voltammetric response of CM at the pH value chosen was practically stable to at least 1 day, with a maximum decrease of less than 1.2 % being quite satisfactory for analytical purpose. Thus, these results clearly indicate that the proposed electrochemical method of analysis is reliable for the determination of CM pesticide.

Interferences: We have also studied the effect of the presence of other pesticides on the shape of the CM reduction peak. In our previous works, a number of pesticides had been studied. As we known, carbamate pesticides⁷ have not electroactivity on the mercury electrode. Organophosphorus pesticides, such as parathion methyl, fenitrothion and parathion⁴, have voltammetric peaks with peak potentials at about -310 mV in the same experimental condition, while phoxim²²,

TABLE-1
CHARACTERISTIC OF THE CALIBRATION CURVES ESTABLISHED USING DIFFERENT DEPOSITION TIMES

(s)	Deposition time equation ^a	Linearity range (ng mL ⁻¹)	RSD for slope	RSD for intercept	Correlation coefficient	LOD ^b (ng mL ⁻¹)
90	I = 0.213c + 0.51	1.0-15	0.23	0.15	0.9956	0.580
150	I = 0.421c + 0.37	0.5-8.0	0.35	0.19	0.9978	0.120
300	I = 0.656c + 0.12	0.5-5.0	0.45	0.25	0.9970	0.098

^aPeak height (I) in nA, concentration (c). ^bJ.N. Miller and J.C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, Pearson Education Limited, London, edn. 4, p. 122 (2000).

thiram²³ and zineb (maneb)²⁴ at -280, -600 and -610 mV, respectively. They did not interfere with the determination of chinomethionate.

Applications: Determination of CM in spiked fruit samples was performed using the standard addition method. Apple and pear were treated as described in experiment and then three different concentrations of the final extract were transferred to the electrochemical cell for analysis as described in experiment. Fig. 4 shows the voltammograms for a spiked apple sample before and after the standard addition. According to the calibration, the concentration of CM in the apple sample is 0.20 ng mL⁻¹, which roughly correspond to 0.6 µg kg⁻¹ in the apple sample. So this value is too low to be quantitatively detected (not in the linear range of determination, Table-1). The recoveries on addition of known amounts of CM to the fruit samples are also given in Table-2. The recoveries were found to be in the range 89.33-98.00 % and the relative standard deviation of 2.8-4.5 %. From these results, it is evident that the developed DPSV procedure can be reliably used for the determination of CM in fruit samples.

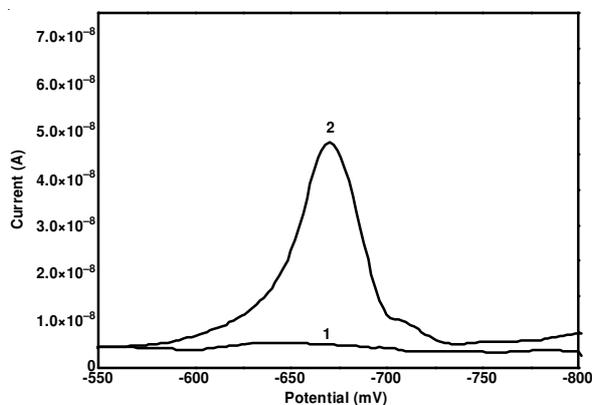


Fig. 4. Differential pulse stripping voltammograms. Curve 1: CM contained in unspiked apple sample; curve 2: after a standard addition, which correspond to 4.71 µg kg⁻¹ in the apple sample

TABLE-2
RECOVERY STUDY OF CHINOMETHIONATE
IN FRUIT SAMPLES^a

Sample	Amount of CM added (µg kg ⁻¹)	Amount of CM found (µg kg ⁻¹)	Recovery (%)	RSD (%)
Apple	5	4.71 ± 1.1 ^b	94.20	3.2
	10	9.52 ± 0.8	95.20	2.8
	20	19.6 ± 0.8	98.00	4.4
Pear	7.5	7.01 ± 1.2	93.47	4.5
	15	13.4 ± 0.6	89.33	3.4
	25	24.3 ± 0.9	97.20	3.0

^aAll the fruit samples are from the market in Nanchang city, China.

^bMean ± SD (n = 5).

Conclusion

Chinomethionate in fruits is normally determined by chromatographic method. The paper describes a new DPSV method for the quantitative determination of chinomethionate. It was found to be simple and highly sensitive. A detection limit of 0.12 ng mL⁻¹ was experimentally obtained. The method can be used successfully to assay the pesticide in spiked fruit samples and can be applied by the environmental quality control laboratories.

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