Asian Journal of Chemistry; Vol. 24, No. 11 (2012), 4971-4974

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Behaviour and Quantification Studies of Iron(III)-dimethyldithiocarbamate Using Cyclic and Square-Wave Stripping Voltammetry

P. Qiu

Department of Chemistry, Nanchang University, Nanchang, P.R. China

Corresponding author: Tel: +86 791 83969514; E-mail: pingqiu@ncu.edu.cn

(*Received*: 3 September 2011; *Accepted*: 6 June 2012) AJC-11540

The adsorptive and electrochemical behaviour of iron(III)-dimethyldithiocarbamate (ferbam) at mercury electrode were explored in Britton-Robinson buffer(B-R) solution by using cyclic and square wave voltammetry. Cyclic voltammetric studies indicated the reduction of iron(III)-dimethyldithiocarbamate at the electrode surface through a single three-electron and three-proton irreversible step and fundamentally controlled by adsorption. The solution conditions and instrumental parameters were optimized for the determination of the authentic food by square wave stripping voltammetry. Iron(III)-dimethyldithiocarbamate gave a sensitive adsorptive reduction peak at -680 mV (*versus* Ag/AgCl). The reduction peak was used to determine iron(III)-dimethyldithiocarbamate in range 1 to 15 ng mL^{-1} with a detection limit of 0.6123 ng mL^{-1}. The procedure was successfully applied for the assay of iron(III)-dimethyldithiocarbamate in real samples.

Key Words: Ferbam, Square wave voltammetry, Hanging drop mercury electrode, Pesticide analysis.

INTRODUCTION

Iron(III)-dimethyldithiocarbamate (ferbam) was originally evaluated in 1965 (toxicology) and 1967 (toxicology and residues) and is included in the dithiocarbamate group. Ferbam is a broad spectrum fungicide for the control of certain diseases in fruit trees, small fruits and berries, potatoes, ornamentals, conifers and tobacco. However, high level of ferbam in foodstuffs may result in serious health problem for human. Therefore, prevention of the negative effects of ferbam requires a systematic control of the content of their remains in agricultural products, food, fodder, soil and water.

Several analytical methods for the determination of ferbam have been reported including UV-spectrophotometry[1,2], chromatography[3,4] and capillary electrophoresis techniques[5]. The electrochemical methods have not been properly explored for the determination of ferbam in spite of their simple set up and high sensitivity and no attempt has been made to determine ferbam in food samples.

Polarography and voltammetry can be considered as a convenient alternative to these routinely employed analytical methods. They permit a direct, simple and rapid determination which requires a minimum volume of sample. Modern square-wave voltammetry is a complex but powerful technique that requires microcomputer and a micro-processor. Most of the recent new instruments can fulfill these conditions and therefore, the technique has become a common and powerful one in determining many organic or inorganic substances[6,7].

Stripping voltammetry is very sensitive method for the determination of many traces of organic compounds and metal ions, which can achieve low level of detection by combining an accumulation process with a voltage scanning measurements[8-12]. Over the last decade, adsorptive stripping voltammetry has become a reliable analytical technique, which is widely applied as one of the most sensitive methods in electroanalytical chemistry.

To date no stripping nor square-wave voltammetric procedures for the assay and quantification of iron(III)-dimethyldithiocarbamate (ferbam) are reported in literature. Hence, the current eletroanalytical research aimed to study the square-wave voltammetric behaviour of ferbam and its interfacial adsorptive accumulation onto the hanging mercury drop electrode. Based on the results obtained, a simple, sensitive and low cost voltammetric procedure was developed for the direct determination of ferbam in food samples.

EXPERIMENTAL

All stripping and cyclic voltammetric measurements were performed with Bioanalytical Systems (BAS, USA) equipped with a PAR 303A cell stand (EG and G); the three-electrode cell contained a hanging mercury drop electrode (HMDE) as the working electrode, an Ag-AgCl (BAS MF 2020) reference electrode and a platinum wire auxiliary electrode. All experiments were carried out at 20 ºC.

All chemicals used were of analytical reagent grade and were used without further purification. Ferbam was obtained from Chem service (West Chester, PA, USA). Stock solution of 100 mg L^{-1} was prepared by dissolving the appropriate amount in methanol in 100 mL volumetric flask. Standard solution was then diluted to the required concentrations with distilled water. A Britton-Robinson (B-R) buffer solution of pH 6.8 was prepared by adding 50 mL of 0.2 mol L^{-1} sodium hydroxide solution into 100 mL of a mixed acid, containing 0.04 mol L^{-1} of each of boric, orthophosphoric and acetic acid[13].

A suitable amount of ferbam solution, together with 2 mL pH 6.8 Britton-Robinson buffer solution was transferred to an electrochemical cell and diluted to 10 mL with distilled water. The solution was purged by purified nitrogen gas for 360 s. After a 10 s static period, a square wave voltammetry scan was run from -400 to -1000 mV at the hanging mercury drop electrode with a scan rate of 20 mV s^{-1}. Table-1 contains the optimum operational parameters selected for the determination of ferbam by square wave stripping voltammetry using hanging mercury drop electrode.

TABLE-1
OPTIMUM OPERATIONAL PARAMETERS SELECTED FOR THE DETERMINATION OF FERBAM BY SWSV AT HMDE

Parameter	Selected value
Accumulation potential	0.00 V
Final potential	+1.3 V
Modulation time	10 s
Frequency	50 Hz
Scan increment	2 mV
Accumulation time	150 s
pH	6.8
Supporting electrolyte	Britton-Robinson buffer

RESULTS AND DISCUSSION

Electrochemical behaviour of ferbam: The cyclic voltammetric behaviour of 10 ng mL^{-1} ferbam in Britton-Robinson buffer pH 6.8 at the hanging mercury drop electrode yielded a single well-defined peak at -725 mV attributed to the reduction of the ferbam. Weak oxidation peak was observed in the positive scanning half-cycle, indicating the irreversible nature of the electrode process. As can be seen from Fig. 1, a substantial decrease of the monitored electrochemical signal was observed in subsequent repetitive scans. Such behaviour indicated rapid adsorption of ferbam from the working electrode surface. Moreover, a straight plot by plotting peak intensity versus scan rate also can be confirmed[14]. The voltammetric cycles carried out for increasing scan rate values over the range 50-1000 mV s^{-1} gave rise to an electrochemical response with increased peak current intensities. The linear relationship between the peak current and the scan rate shows that the reduction process is adsorption-controlled. The plot of log ip *versus* log v, gave a straight line with slope value of 1.09, which is close to the theoretical value of 1.0 expected for the interfacial adsorptive character of ferbam on to the surface electrode[15]. In addition, the observed peak potential shifts to a more negative value with the increase of scan rate, which confirmed the irreversible nature of the studied reduction process.

Linear scan voltammetry is often used to investigate the behaviour of electrochemical systems. In this study, the variation of the linear scan voltammetry peak current of ferbam *vs*. the square root of the scan rate was examined (Fig. 2). A deviation from linear to a parabolic trend can be observed if the preconcentration time is 15 or 150 s, which shows that the process is controlled by adsorption[16].

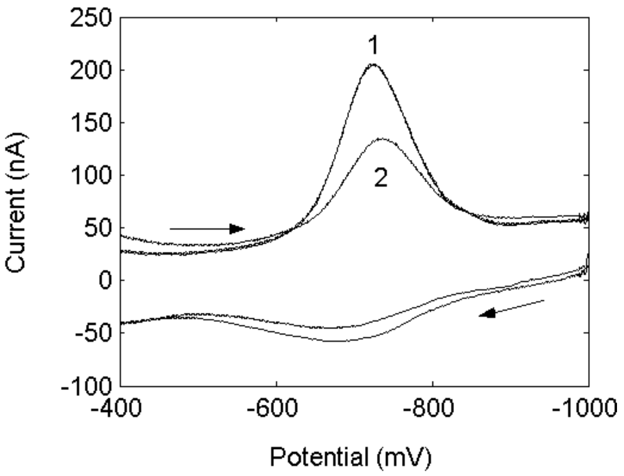

Fig. 1. Repetitive cyclic voltammograms for 10 ng mL^{-1} ferbam in pH 6.8 B-R buffer and scan rate 100 mV s^{-1}

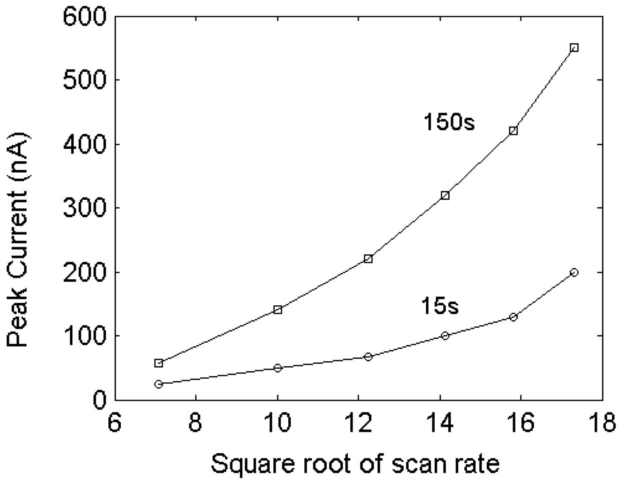

Fig. 2. Effect of square root of scan rate on the peak current at different preconcentration times. Instrumental parameters as in Fig. 1

The strong adsorption phenomenon of ferbam can be used as an effective preconcentration step prior to the actual voltammetric quantification of the analyte. The adsorptive stripping voltammetric response of ferbam at hanging mercury drop electrode was examined in Britton-Robinson buffer pH 6.8 using the differential pulse (DP) and square wave (SW) excitation waveforms. The electrochemical current intensity for the reduction of ferbam recorded by the square wave voltammetric technique was nearly 2 times higher than that generated by the differential pulse excitation mode (Fig. 3). Due to its intense sensitivity, therefore square wave stripping voltammetry approach was used in all the subsequent experiments.

Optimum parameters and experimental conditions: Among the investigated supporting electrolytes (acetate, phosphate, carbonate and Britton-Robinson buffers), the ideal stripping voltammetric peak including its high sensitivity and well resolution have been observed when using B-R buffer solution. Since the acidity of the buffer solution is also an important parameter to be optimized in the stipping voltammetry, the effect of pH on the reduction of ferbam at hanging mercury dropping electrode was studied over the pH range 1.8-11.9 at the concentration 4 ng mL^{-1} ferbam by square wave stripping voltammetry as shown in Fig. 4. A small current was observed at pH3.5, which increased gradually up to pH 6.2 and then decreased at higher pH. Thus, pH 6.8 was used in all measurements. A gradual shift to more negative potential was observed when varying pH value over the range 2-9, indicating consumption of H$^+$ in the electrochemical reduction process.

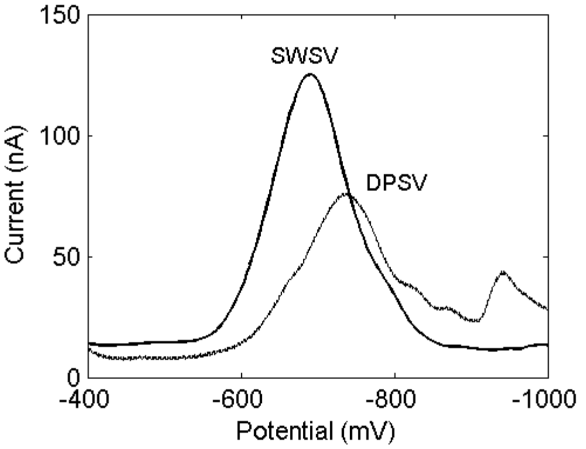

Fig. 3. Adsorptive voltammograms of 4 ng mL^{-1} ferbam in B-R buffer (pH 6.8) obtained by: DPV (v = 20 mV s^{-1}, E_{DP} = 25 mV); SWV (f = 50 Hz, Δs = 2 mV) after the preconcentration of 150s at E_{acc} = 0 V

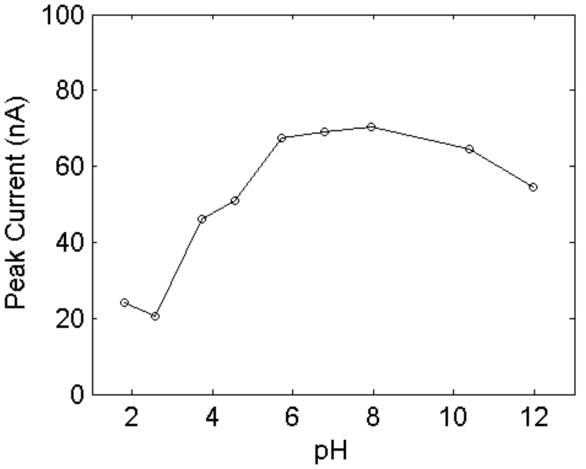

Fig. 4. Influence of pH on the peak current for 4 ng mL^{-1} ferbam solutions

For 4 ng mL^{-1} ferbam solution, the peak current increased with increasing analyte pre-concentration time. However, at approximately 150 s the peak current began to level off (Fig. 5). The adsorption of ferbam on the surface of the mercury electrode is approaching equilibrium. Thus, for further square wave stripping voltammetry quantitative studies for ferbam, 150 s was chosen as the optimum analyte pre-concentration time since it provided relatively high peak current with adequate practical time.

In addition, the preconcentration potential is a major factor affecting the response sensitivity. When the influence of preconcentration potential on the observed stripping voltammetric signal was examined over the range of -0.6 to + 0.2V at 150 s accumulation time, the peak current increased steadily over the positive direction till it reached its maximum value at E_p = 0.0 V where it decreased sharply thereafter. Hence, for optimal analytical sensitivity this experimental parameter was maintained at 0.0 V.

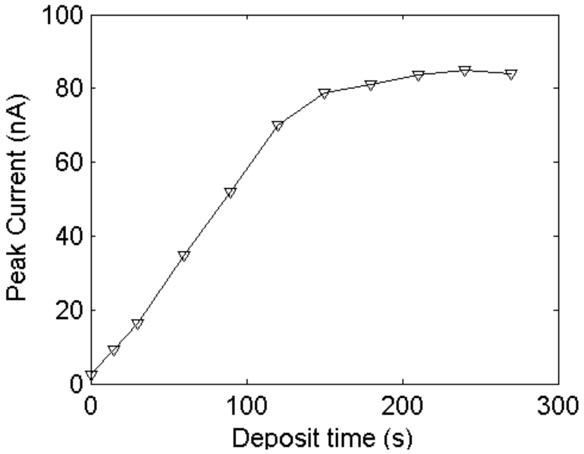

Fig. 5. Effect of the accumulation time on the voltammetric peak height

Mechanism of electrode reaction: The square wave frequency equation for an irreversible electrochemical reaction is $\Delta E_p/\Delta \log f = -2.303\ RT/\alpha nF$[17], where f is frequency of square wave, α is the transfer coefficient and n is the number of electrons transferred. According to the equation: $E_p(mV) = -720 - 0.041 \log f\ (Hz)$, the slope of this straight line, $\Delta E_p/\Delta \log f$ value, was estimated to be 0.041, which on substitution into the above equation gave a value of 1.445 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 reaction studied is equal to 3.

Combining the information and the work of Lin *et al.*[18], the mechanism of this electrochemical reaction can be represented by a chemical equation (Fig. 6) involving three electrons, three protons, which will cause the addition of three protons to the thio groups. Also, the geometric structure of ferbam will be changed when the reductive process occurs. Both the carbon disulfide groups will be distanced from each other and loss the capability of chelating to the Fe^{3+} ion. In consequence the Fe^{3+} ion will be free from the carbon disulfide groups to the bulk solution.

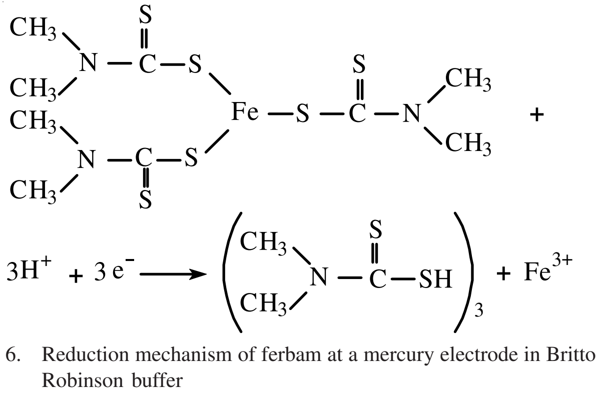

Fig. 6. Reduction mechanism of ferbam at a mercury electrode in Britton-Robinson buffer

Calibration graph and detection limit: A linear calibration graph (r = 0.998) for ferbam was obtained by square wave stripping voltammetry in the 1 ng mL^{-1} to 15 ng mL^{-1} concentration range, with a slope of 27.256 nA mL ng^{-1} and an intercept of -0.5626 nA. A limit of detection of 0.6123 ng mL^{-1} was determined according to the method described by Miller and Miller[19].

Accuracy, precision and stability: The accuracy of the proposed method was checked by calculating the recovery of known amount of ferbam (4 ng mL^{-1}) added to B-R buffer solution and analyzed *via* the optimized stripping voltammetric procedure. The value of the mean recovery obtained by the standard addition method was 101.2 % with standard deviation of 1.31 % (the analytical measurements repeated five times). The analytical precision of the developed method was verified from the reproducibility of 10 determinations of 4 ng mL^{-1} ferbam and the estimated relative standard deviation (R.S.D. %) was 1.25 %. Finally, when the square wave stripping voltammetry signal of 4 ng mL^{-1} ferbam solution was monitored every 15 min, it was found to be nearly stable for a period of at least 2 h.

Interference: The preliminary possible interferences study was investigated by the addition of various amount of interference substances at the presence of 4 ng mL^{-1} ferbam, other operational conditions are same as those in Fig. 3. The interference substances used in this investigation include thiram, maneb, disulfiram, ziram, zineb and captafol, all of them used as thiocarbamate fungicides. Under the same experimental conditions used for ferbam, voltammograms from solutions of all these compounds showed well-defined reduction peaks at potentials close to that of ferbam. In our previous work, it is found that their peak potentials are at -610, -640, -648, -584, -1160 and -900 mV, respectively. Thus a good potential resolution from voltammetry is observed. The influence of other coexisting interference on square wave stripping voltammetry determination of ferbam was investigated. Ten-fold amounts of ferbam, Mn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} did not interfere in the square wave stripping voltammetry determination of ferbam. If Fe^{3+} present with ferbam, it will interfere with the determination. However, the interference can be avoided by the re-extraction of ferbam into chloroform, in which Fe^{3+} remained in the aqueous phase and the ferbam entered chloroform. Ferbam can be determined by the general procedure after evaporation of the organic solvent to dryness.

Determination of ferbam in commercial samples: 10 g of the sample were crushed with a pestle and mortar and shaken mechanically with 100 mL chloroform for 1 h. The mixture was filtered and the residue in the funnel was washed with chloroform. The extracts were evaporated down to 2 mL in a water bath (80-90 ºC) and the remaining solvent was removed in a current of dry air at room temperature. The residue was dissolved in methanol and ferbam was determined by the general procedure. In this work all the spiked crop samples were determined by the proposed method, square wave stripping voltammetry and HPLC[4]. The results obtained by both techniques are in good agreement each other (RSD < 4.0 %) (Table-2).

TABLE-2
DETERMINATION OF FERBAM IN SAMPLES

Crop[a]	Ferbam added (µg)	Ferbam found (µg)[b]			
		Proposed method	RSD (%)	Method of ref.[4]	RSD (%)
Peanut	5	4.7	2.1	4.8	2.0
	20	19.1	3.2	19.0	2.0
	40	38.3	2.8	38.0	2.2
Rice	5	4.6	3.3	4.8	1.9
	20	18.6	2.5	18.1	2.3
	40	38.1	3.5	38.1	2.7
Wheat	5	4.7	3.4	4.8	2.6
	30	28.9	2.3	28.7	2.5
	50	47.9	2.4	47.8	2.5

[a]All the samples were obtained from a supermarket in Nanchang, China; [b]Average of three experiments

Conclusion

The square wave stripping voltammetry method with the mercury drop electrode for the quantitative determination of ferbam was found to be simple and highly sensitive. A detection limit of 0.6123 ng mL^{-1} at 150 s accumulation time with the standard deviation 1.31 % was obtained in pure solutions. The method can be used successfully to assay the crop samples.

ACKNOWLEDGEMENTS

The author gratefully acknowledged the financial support of this project by the National Science Foundation of China (No. 20865003), the Jiangxi Province Natural Science Foundation (2007JZH2644) and the Jiangxi Province Education Department Science Foundation (GJJ10037).

REFERENCES

1. A.K. Malik and A.L.J. Rao, *Talanta*, **44**, 177 (1997).
2. S. Agarwal, S.G. Aggarwal and P. Singh, *Talanta*, **61**, 871 (2003).
3. E. Brandsteterova, J. Lehotay, O. Liska and J. Garaj, *J. Chromatogr. A*, **354**, 375 (1986).
4. E. Brandsteterova, J. Lehotay, O. Liska, J. Garaj and I. Zacsik, *J. Chromatogr. A*, **286**, 339 (1984).
5. A.K. Malik, B.S. Seidel and W. Faubel, *J. Chromatogr. A*, **857**, 365 (1999).
6. J.G. Osteryoung and R.A. Osteryoung, *Anal. Chem.*, **57**, 101A (1985).
7. P. Ostapczuk, P. Valenta and H.W. Nurnberg, *J. Electroanal. Chem.*, **214**, 51 (1986).
8. O.A. Farghaly, *Microchem. J.*, **75**, 119 (2003).
9. O.A. Farghaly, *Talanta*, **63**, 497 (2004).
10. O.A. Farghaly, *J. Pharm. Biomed. Anal.*, **23**, 783 (2000).
11. A.M.M. Ali, O.A. Farghaly and M.A. Ghandour, *Anal. Chim. Acta*, **412**, 99 (2000).
12. O.A. Farghaly, H.M.A. El-Wadood and M.A. Ghandour, *J. Pharm. Biomed. Anal.*, **21**, 233 (1999).
13. D.D. Perrin and B. Dempsey, Buffers for pH and Metal Ion Control, Chapman and Hall, London, 155 (1974).
14. A.M. Bond, Modem Polarographic Methods in Analytical Chemistry, Marcel Dekker, New York (1980).
15. E. Laviron, *J. Electroanal. Chem.*, **112**, 11 (1980).
16. A.J. Bard and L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York (1980).
17. M. Lovric, S. Komorsky-Lovric and R.W. Murray, *Electrochim. Acta*, **33**, 739 (1988).
18. M.S. Lin, B.I. Jan, H. Leu and J.S. Lin, *Anal. Chim. Acta*, **388**, 111 (1999).
19. J.N. Miller and J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, Pearson Education Limited, London, edn. 4, 122 (2000).