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ELETROANALYTICAL METHODS FOR DETECTION OF THE FUNGICIDE, COPPEROXYCHLORIDE

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ABSTRACT

Potentiometric electrode consisting of a thin copper wire is used to determine the fungicide, Copper oxychloride, in aqueous chloride medium with a high sensitivity and selectivity. Sensitivity of detection is further improved by employing an amperometric method based on a bare glassy carbon disk electrode. Levels of interference of common environmental species and agrochemical constituents are not significant indicating the reliability of analytical results of a complex mixture. Noise of electrochemical signals can be minimized by surface modification of glassy carbon electrodes.

Keywords: Copper oxychloride, fungicide, detection, electroanalysis.

1. INTRODUCTION

The fungicide, Copper oxychloride (dicopper chloride trihydroxide) is currently used as a protective fungicide. Some common applications of this fungicide are to control anthracnose and cercospora leaf spot on vegetables, chilies, tobacco and cloves; coffee rust; late blight and early blight on tomatoes and potatoes; and blister blight on tea. It is available with the trade names of Recop, Cupravit, Fernacot, Pere-col and Helmoxy[1].

The determination of Copper oxychloride in environmental samples has been conducted by monitoring the copper content of residues using colorimetric or atomic absorption spectroscopic methods[2]. Although colorimetry is a basic tool in environmental analysis due to simplicity and economical factors, it lacks the sensitivity of detection. Consequently, low levels of Copper oxychloride cannot be detected using colorimetric methods with a high accuracy. On the other hand, atomic absorption methods with the flame atomizer offer a lower detection limit in the range of $\mu g\ dm^{-3}$ for copper; however, this methodology is not economical and instrumentation is complex.

Electroanalytical methods, in particular, potentiometric and amperometric procedures, offer several advantages over the conventional methods stated earlier. They are not only economical and simple, but also selective and sensitive[3,4]. Consequently, these techniques have already been used for determination of several organic and inorganic environmental pollutants[5-10], and metal ions[11-13] at bare or modified electrodes.

Electrochemical behaviour of copper disk electrodes and copper film deposited electrodes in aqueous medium has been reported by numerous research groups. The fate of copper species and the effect of anions on the formation of different copper complexes in aqueous medium have also been well documented[14-20]. Deposited copper species have been used as a reagent for selective determination of chlorine species at low levels[18]. Despite the number of reports on corrosion, passivation, underpotential deposition and mechanistic studies of copper, analytical utility based on the electrochemistry of copper species, especially, for environmental analysis has not been widely addressed.

This paper reports two simple methods for detection of Copper oxychloride in aqueous medium based on copper(II) detection. The first method is a potentiometric determination with a copper wire electrode, and the second is an amperometric determination with a bare glassy carbon electrode. The interferent effects of other agrochemicals, and some soil and fertilizer constituents on the electrochemical determination of Copper oxychloride are also described. Additionally, possibility of employing modified glassy carbon surfaces in order to decrease noise levels of amperometric responses is addressed.

2. EXPERIMENTAL

2.1 Materials

Hydrochloric acid and nitric acid supporting electrolytes were purchased from Aldrich Chemical Company, USA. A sample of Helmoxy [50% w/w Copper oxychloride-$ClCu_2(OH)_3$] was gifted from Heychem Ltd., Sri Lanka and used for all electrochemical measurements without any purification. The compound, 5,10,15,20-tetraphenylporphine free base [H_2TPP] was synthesised according to the published procedure[21]. The substances; K_2SO_4 (BDH), $CaCl_2$ (BDH), $ZnCl_2$ (BDH), $MgCl_2$ (Vickers), $FeCl_3$ (Park), H_3PO_4 (BDH), KNO_3 (Vickers), $MnSO_4$ (BDH), Endosulfan (Cepetco, Sri Lanka), Chlorpyrifos (Anglo Asian Ltd., Sri Lanka), and Trichlorfon (Bayer) were selected as interfering species. They were used as received and treated under the same experimental conditions as used for Copper oxychloride. Electrolyte solutions for all experiments were prepared in freshly distilled water, and deaeration of the solution was accomplished by sparging with nitrogen before voltammetric and amperometric experiments.

2.2 Instrumentation

An ion analyzer (Corning Model 250) was used in all potentiometric studies with the copper wire working and the saturated calomel (SCE) reference electrodes. CV-1B cyclic voltammograph in combination with the BAS X-Y recorder (both from Bioanalytical Systems, USA) was used for cyclic voltammetric and amperometric experiments. These measurements were made using a three electrode system consisting of a glassy carbon disk working (BAS, USA), a SCE reference and a platinum wire counter electrodes. Potential in all experiments were reported with respect to SCE.

2.3 Electrode Preparation

Copper wire electrodes were cleaned by mechanical polishing with alumina slurry followed by rinsing with distilled water. Glassy carbon (GC) electrodes were cleaned by polishing with alumina slurry on a home-made polishing pad for about 30 sec. Then the GC electrode was rinsed with distilled water followed by sonication in an ultrasonic bath for five minutes and rinsed again with distilled water. The cleaned copper wire and GC electrodes produced reproducible results and more sophisticated cleaning procedures were not attempted.

The cleaned GC electrode was rinsed with a few drops of distilled dichloromethane and air dried before surface modification. Two drops of the $5x10^{-4}$ mol dm^{-3} coating solution, which was prepared by dissolving an appropriate amount of the coating material (H_2TPP) in distilled dichloromethane, were introduced on to the dry electrode surface. A sufficient time was allowed to evaporate the solvent, and the modified GC electrode was then equilibrated in the electrochemical cell before voltammetric and amperometric experiments.

3. RESULTS AND DISCUSSION

3.1 Potentiometric Studies

Potentiometric experiments conducted with a series of fungicide solutions prepared in 0.1 mol dm^{-3} HCl and in 0.1 mol dm^{-3} HNO_3 electrolytes showed linear dynamic ranges from 1×10^{-3} mol dm^{-3} to 5×10^{-6} mol dm^{-3} and 1×10^{-3} mol dm^{-3} to 5×10^{-5} mol dm^{-3} respectively, according to the calibration plots of potential (E) vs. log C, where C is the bulk concentration of copper(II) in fungicide solutions (Fig. 1). Potentiometric measurements are based on the selective determination of Cu(II) at a copper wire electrode. Copper electrode in a solution of Cu(II) is found to be an equilibrium system, if there are no stabilizing agents for Cu(I) species present in solution[17].

The analyte, Copper oxychloride, is preferentially soluble in either acidic or basic media, and consequently, common neutral electrolytes such as NaCl and KCl are not suitable for this study. Although the analyte is soluble in any acidic medium, HCl was selected as the medium of choice for all experiments as it offers lower limits of detection (Fig. 1). This selection is in agreement with previous reports on copper electrodes in the presence of chloride ions being sensitive to Cu(I) ions at concentrations as low as 10^{-9} mol dm^{-3}. Therefore, the determination of Cu(II), the oxidation state of copper in the analyte, would also be more sensitive in chloride electrolytes. The concentration of chloride ions in the medium was kept constant for reproducible measurements, because Cu(II) ions form different chloro-complexes with Cl^- ions as shown below[17].

$$Cu^{2+} + m\,Cl^- \rightleftharpoons CuCl_m^{2-m}\ (m = 1\text{-}4) \tag{1}$$

Although the proposed potentiometric detection is sensitive to the 10^{-6} mol dm^{-3} range (ca. 65 μg dm^{-3} Cu), further improvement of sensitivity can be achieved with amperometric procedures. In order to select an appropriate potential for amperometric detection, a series of cyclic voltammetric experiments should be conducted.

3.2 Cyclic Voltammetric Studies

Cyclic voltammetric experiments of the Helmoxy fungicide formulation (5×10^{-3} mol dm^{-3} in Copper oxychloride) prepared in either 0.1 mol dm^{-3} HCl or in 1.0 mol dm^{-3} NH_4OH electrolyte showed the expected electrochemistry of Cu(II) in aqueous medium as reported by many researchers (Fig. 2)[15,20].

The voltammetric peaks observed in Fig. 2 can be assigned for Cu(II)/Cu(I) [peaks 1 and 2] and Cu(I)/Cu(0) [peaks 3 and 4] processes based on thermodynamic arguments. Although the amperometric determination of Cu(I) may be more sensitive than Cu(II) according to observed peak currents, it would not be a good choice for amperometric detection of Copper oxychloride as the deposition of Cu(I) and subsequent stripping of metallic Cu [peaks 3 and 4] are not diffusion-controlled processes, which would lead to irreproducible results.

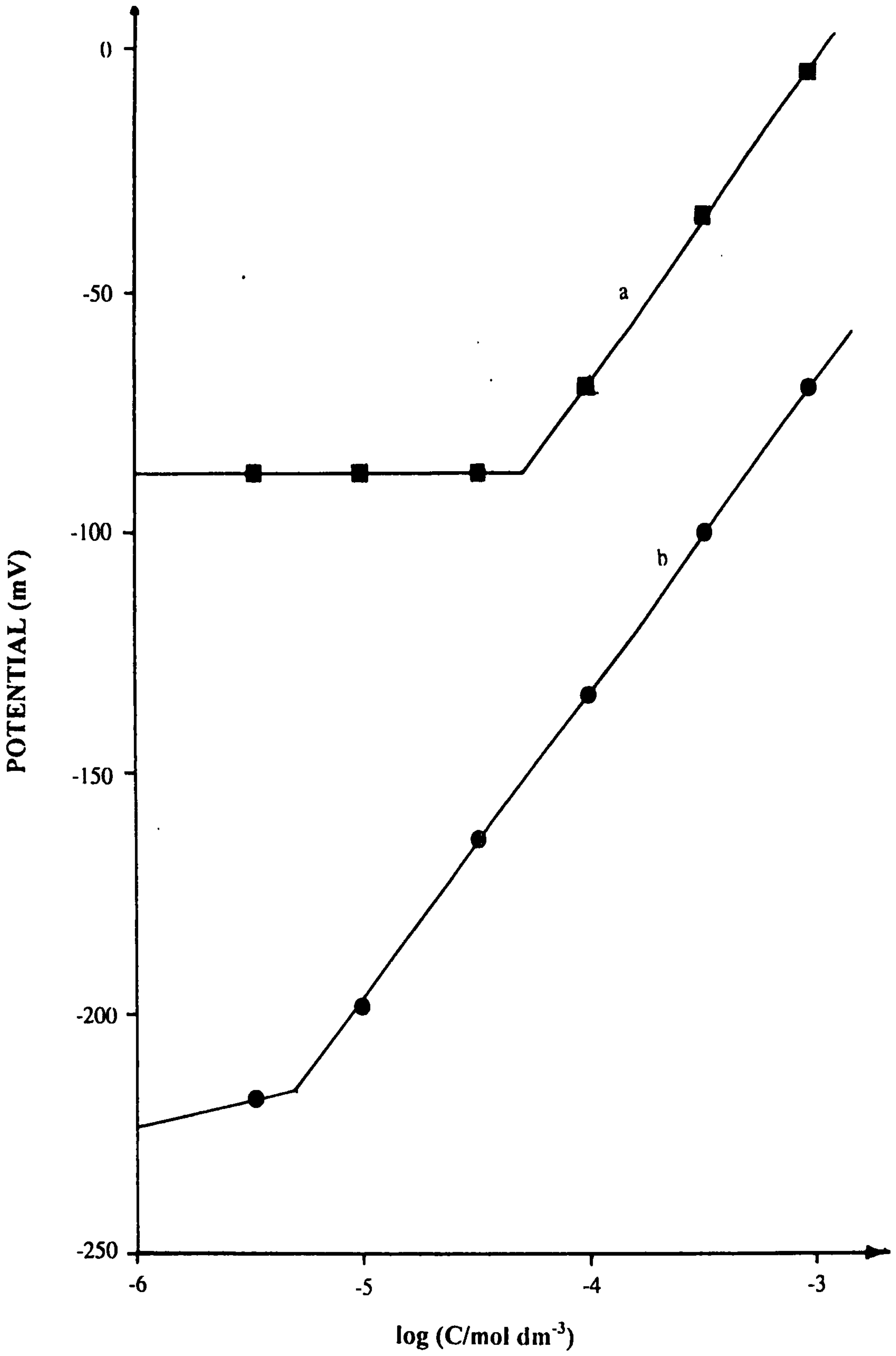

Fig. 1. Potentiometric calibration curves [potential (E) vs. log C] of the fungicide, Copper oxychloride at bare copper wire electrode under air satd. in (a) 0.1 mol dm^{-3} HNO_3 (b) 0.1 mol dm^{-3} HCl

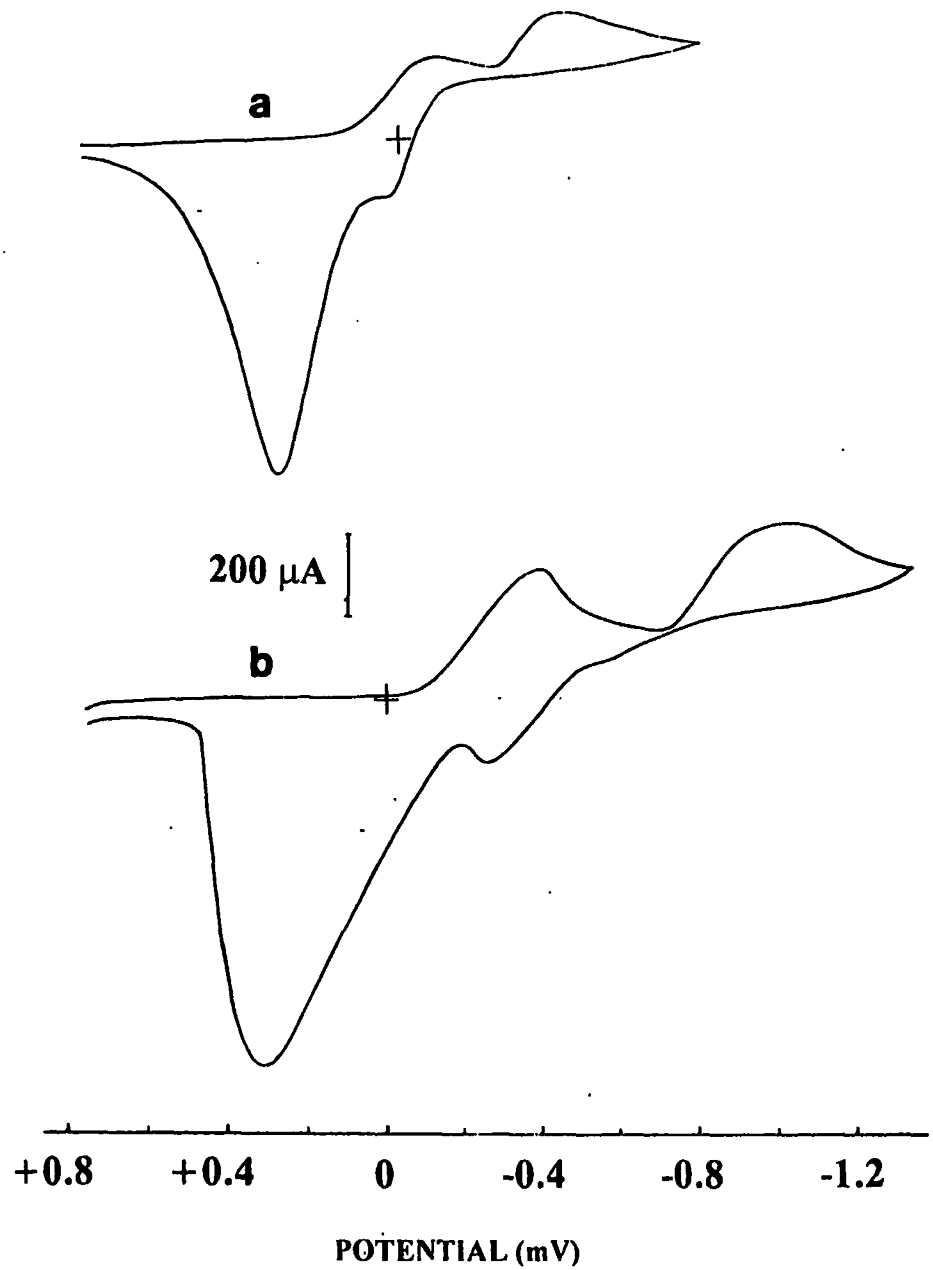

Fig. 2. Cyclic voltammograms of bare GC electrode of the Helmoxy fungicide formulation [5×10^{-3} mol dm^{-3} Copper oxychloride] under N_2 satd. Scan rate 100 mV s^{-1}. Supporting electrolyte (a) 0.1 mol dm^{-3} HCl (b) 1.0 mol dm^{-3} NH_4OH.

3.3 Amperometric Studies

Potential of operation for amperometric detection should be optimized in order to obtain sensitive and reproducible results. In this regard, several potentials were selected in the vicinity of the reduction peak of Cu(II)/Cu(I) [peak at -0.10 V in the acidic medium] for preliminary investigation. The amperometric response at -0.10 V shows a higher noise than that observed at -0.15 V (Fig. 3). On the other hand, the more negative potentials of -0.20 V and -0.25 V result in lower sensitivities together with some noise. These potentials may also have complications due to the overlap with the second reduction peak (peak 3). Furthermore, potentials below -0.10 V would have an overlap with the stripping peak (peak 4) according to Fig. 2. Thus, an operational potential of -0.15 V is recommended for analysis of the fungicide in aqueous acidic medium.

The linear dynamic range of amperometric studies at all the attempted potentials is approximately the same; 5×10^{-7} mol dm^{-3} to 6×10^{-6} mol dm^{-3} (Fig. 3). Furthermore, the minimum detection limit at -0.15 V was estimated to be in the order of 10^{-8} mol dm^{-3} based on the signal-to-noise ratio of 3. This is equivalent to a concentration of 2 μg dm^{-3} (ppb) copper which is a significant improvement over the traditional colorimetric and the proposed potentiometric procedures. Thus, the proposed amperometric method would be used to detect small amount of the fungicide, Copper oxychloride in environmental samples. Another interesting feature of the proposed detection is the accessibility of such a low detection limit using neither modified electrodes nor catalytic materials. Furthermore, reproducible results were obtained at the bare electrode concluding that adsorption processes have not occurred on the bare electrode at the potential of operation. Noise levels of amperometric responses can be decreased by modifying the bare glassy carbon surface with electroinactive materials. In this regard, the macrocyclic chelating agent, 5, 10, 15, 20-tetraphenylporphine [H_2TPP], was selected. This would result in a change in the rate of electron transfer between copper ions and the carbon electrode surface forming a coordination complex, or alternatively, it would act as a diffusion barrier between the bulk species and the electrode surface.

3.4 Interference Studies

Although bare Cu wires or bare GC electrodes are used in the proposed detection, they encounter only a few interferent problems. Common cationic and anionic constituents present in soil, chemical constituents of fertilizer and several agrochemicals were introduced into the electrochemical cell in the laboratory in order to study the effect of interferent species on the detection of the fungicide. All interfering species showed a negligible potential-concentration dependence in potentiometric measurements (Fig. 4) and little or no current in amperometric measurements (Table 1) with the exception of Fe(III) species, which shows about 10% of the Copper oxychloride response. Interaction of copper and ferric ions has already been observed in chloride electrolyte solutions which would support our experimental observations[16].

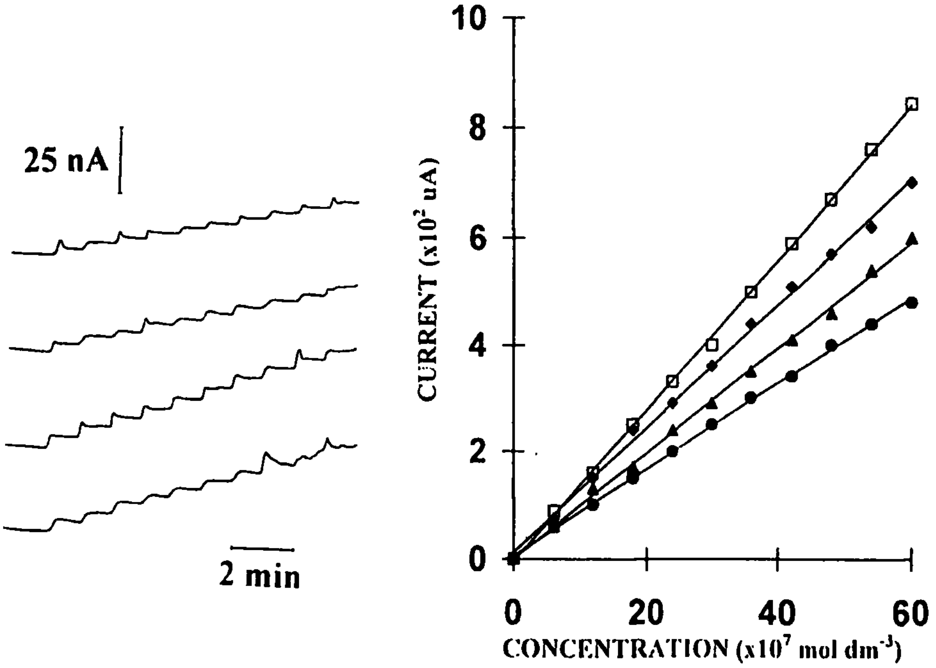

Fig. 3. Amperometric current-time responses obtained with the bare GC electrode with increasing concentrations of Copper oxychloride in 0.60 umol dm^{-3} steps under N_2 satd (left), and corresponding calibration curves (right). Applied potential (a) -0.15 V (b) -0.10 V (c) -0.20 V (d) -0.25 V.

Table 1. Comparison of amperometric responses of possible interferent species, introduced at 1x10^{-3} mol dm^{-3} concentration.

Species	i_p(um)	$^*i_{p(int)}/i_{p(analyte)}$
Copper oxychloride	1.66x10^{-1}	1.0
Fe^{3+}	1.69x10^{-2}	1.0x10^{-1}
Ca^{2+}	-	-
Mg^{2+}	-	-
Zn^{2+}	-	-
Mn^{2+}	-	-
NO_3^-	-	-
F^-	-	-
PO_4^{3-}	1.25x10^{-3}	7.5x10^{-3}
SO_4^{2-}	-	-
Endosulfan	-	-
Chlorpyrifos	-	-
Trichlorfon	-	-

* $i_{p(int)}$ = Steady-state current of each interferent; $i_{p(analyte)}$ = Steady-state current of Copper oxychloride.

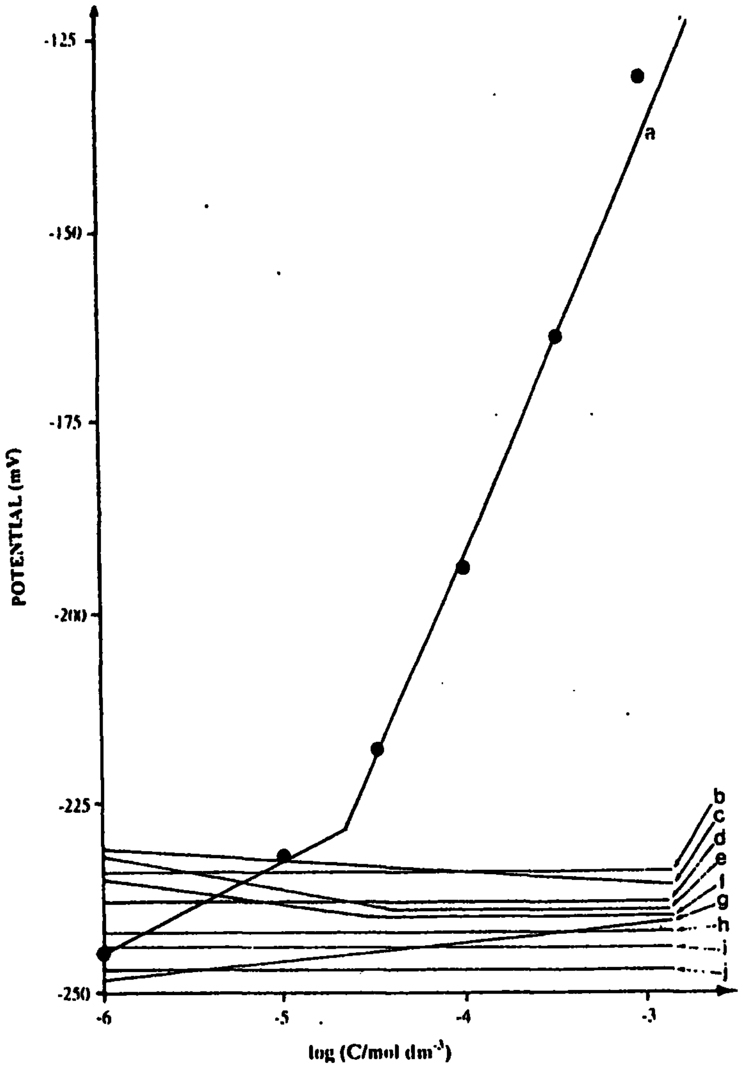

Fig. 4. Potentiometric responses at the bare copper wire electrode under air satd. in the presence of interferent species at varying concentrations. Supporting electrolyte 0.1 mol dm^{-3} HCl. Note that the potential axis has been expanded as compared to that of Fig. 1. Interferent species (a) Fe^{3+} (b) Ca^{2+} (c) SO_4^{2-} (d) PO_4^{3-} (e) Endosulfan (f) NO_3^- and Chlorpyrifos (g) Trichlorfon (h) Mg^{2+} (i) F^- (j) Zn^{2+}.

Due to this interference, the determination of the fungicide in real environmental samples in the presence of Fe(III) species would cause an error of 10% according to the proposed procedure if both Fe(III) and Cu(II) are present at similar concentration levels. However, this problem can be overcome if Fe(III) species are separated from Cu(II) species, preferably by employing ion-chromatographic procedures where different ions are eluted at different times. Introduction of selective chelating agents for cupric species in the presence of ferric ions would be an alternative approach to solve this problem.

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