

Comparison of Indirect Cathodic Stripping Voltammetric Methods Based on Accumulation of Mercury, Copper(I) and Nickel Salts or Complexes at a Hanging Mercury Drop Electrode: Determination of 2-Mercaptobenzothiazole*

Arnold G. Fogg^a, Razali Ismail^a, Rahmalan Ahmad^b and Florin G. Banica^{a,†}

^a Chemistry Department, Loughborough University, Loughborough, Leicestershire, UK LE11 3TU

^b Chemistry Department, Technical University of Malaysia, Johor Bahru, Malaysia

A preliminary study of the indirect cathodic stripping voltammetric determination of 2-mercaptobenzothiazole (MBT) based on accumulation of its mercury, copper(I) and nickel(II) salts or complexes was made as part of a wider study comparing these three related techniques of determining thiols. Detection limits for MBT using the copper(I) and nickel(II) methods ($< 2 \times 10^{-9}$ mol l⁻¹) are considerably lower than that for the mercury method (about 3×10^{-7} mol l⁻¹). The mercury method is susceptible to interference from copper(II) and large amounts of nickel(II), and seems generally to be less reliable for the determination of MBT. The change from accumulation as the mercury salt to accumulation as the copper(I) salt is illustrated in the presence of excess of MBT over copper(II) with increasing copper(II) concentrations, and with change of accumulation potential to more negative values from +100 mV. In the presence of a stoichiometric amount or excess of copper(II) over MBT, no mercury salt is accumulated at potentials more negative than +50 mV. Currents obtained for MBT with the nickel(II) method are much higher than those obtained previously with cysteine and penicillamine.

Keywords: Cathodic stripping voltammetry; 2-mercaptobenzothiazole; hanging mercury drop electrode; accumulation as mercury, copper(I) and nickel complexes or salts

Introduction

The original cathodic stripping voltammetric (CSV) technique involved the accumulation of compounds, such as thiols, at a hanging mercury drop electrode as their mercury salts, mercury being oxidized at a less positive potential in the presence of compounds that form insoluble salts or complexes.¹ The thiol is determined indirectly by monitoring the reduction of the mercury ion in the salt during the cathodic scan. More recently, CSV has been applied in many other ways, *e.g.*, directly using the reduction of adsorbed metal complexes and organic compounds.¹ In a technique related to the original CSV technique, compounds that form copper(I) complexes or salts

are accumulated as such at or near -0.1 V by adding copper(II) to the analytical solution.¹ The copper(II) is reduced to copper(I) in the presence of the complex or salt-forming compound during accumulation at about -0.1 V. The organic compound is determined indirectly by subsequent reduction of the copper(I) in the salt to copper amalgam during the cathodic scan. This technique has been found to be superior to the mercury method in several applications.

Recently, a CSV technique that can be considered to be related to the mercury and copper(I) techniques, in that it is an indirect method of determining thiols, has been developed based on the use of the catalytic nickel peak at about -0.6 V.^{2–5} The technique is different from the other two methods in three main respects. First, the compound is accumulated in the presence of nickel(II) either as the nickel complex or as the mercury salt. If the mercury salt is accumulated the nickel complex is formed during the cathodic scan when the mercury salt is reduced and the thiol is released. Second, nickel(II) in the complex is reduced with a lower overpotential and the reduction peak of nickel is observed at a less negative potential than that at which hydrated nickel(II) is reduced. Third, the peak is catalytic in that the thiol released when the nickel(II)–thiol complex is reduced can complex and cause the reduction of further nickel ions. The height of the catalytic nickel peak depends on the rate of reduction of the nickel(II) in the complex, the availability of nickel ion at the electrode surface, and the rate of complex formation of the thiol with the nickel ion. In practice, for the thiols studied so far, namely cysteine,² glutathione³ and penicillamine,⁵ the currents obtained have been relatively small, which may indicate that relatively small amounts of the thiol are accumulated at very low bulk concentrations of the thiol rather than its having little catalytic activity. Indeed, the lower detection limit for cysteine relative to that of penicillamine has been used as evidence of the greater catalytic activity of cysteine.⁶

This paper reports a preliminary study of the determination of 2-mercaptobenzothiazole (MBT) by indirect CSV, in which the three methods described above were compared. Derivatives of MBT are used extensively as accelerators in the vulcanization of rubber.⁷ MBT is also used as a corrosion inhibitor in antifreezes based on ethylene glycol: it inhibits corrosion of copper and copper alloys caused by oxygen. Because of its widespread use, MBT has been detected in many environmental samples, including industrial and municipal waste waters. Liquid–liquid extraction and HPLC have been used to determine MBT and its derivatives,⁸ as have polarography and

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† Present address: Norwegian University of Science and Technology, Department of Chemistry, N-7055 Dragvoll, Trondheim, Norway.

voltammetry.^{9,10} Goyal and Kumar¹⁰ studied the oxidation of MBT at a pyrolytic carbon electrode: a platinum ring-disc electrode was used to determine MBT in ethylene glycol samples at 3×10^{-4} – 6×10^{-2} mol l⁻¹ levels. Calusaru⁹ showed that by forming the cobalt(II)–MBT complex, MBT could be determined polarographically at 1×10^{-6} – 1×10^{-5} mol l⁻¹ levels using the catalytic hydrogen peak produced by the complex.

Experimental

CSV was carried out with a Metrohm (Herisau, Switzerland) 646/647 VA processor, using a multi-mode electrode in the hanging mercury drop electrode (HMDE) mode. The three-electrode system was completed by means of a glassy carbon auxiliary electrode and an Ag–AgCl (3 mol l⁻¹ KCl) reference electrode. All potentials are quoted relative to this reference electrode. Differential-pulse voltammetry was carried out with a pulse amplitude of 50 mV, a scan rate of 10 mV s⁻¹ and a pulse interval of 1 s.

Stock solutions of MBT (Aldrich, Gillingham, Dorset, UK) in methanol (3×10^{-3} mol l⁻¹) were prepared fresh every 3 d: more dilute solutions were prepared daily by diluting these solutions with methanol. Standard copper(II) and nickel(II) solutions were prepared daily by diluting standard solutions (Spectrosol, BDH, Poole, Dorset, UK). Britton–Robinson buffer was prepared by dissolving boric acid (5 g), orthophosphoric acid (2.7 ml) and glacial acetic acid (2.3 ml) in water and diluting to 1 l. Appropriate volumes of this solution were adjusted to the required pH with sodium hydroxide solution (1 mol l⁻¹).

The general procedure used to obtain cathodic stripping voltammograms was as follows: a 20 ml aliquot of buffer was placed in the voltammetric cell and the solution was purged with nitrogen for 6 min with the stirrer on. After an initial blank run, the required volumes of MBT and copper or nickel solutions were added by means of a micropipette. After forming a new mercury drop, accumulation was effected for the required time at the pre-determined accumulation potential whilst the solution was stirred. The small mercury drop size was used on the Metrohm 647VA stand. At the end of the accumulation period the stirrer was switched off and after 10 s had elapsed to allow the solution to become quiescent a negative-going potential scan was initiated. When further volumes of MBT solution or reagents were added the solution was de-oxygenated for a further 20 s before producing further voltammograms.

Results and Discussion

As is the case with other thiols, MBT was found to be determinable indirectly by CSV after accumulation as its mercury salt at a HMDE. The peak potential was relatively independent of pH, being between -0.1 and -0.2 V at pH 4–9. Accumulation was most effective at 0 V at pH 4. The detection limit was about 3×10^{-7} mol l⁻¹.

MBT could also be determined as its copper(I) salt/complex. The optimum pH was again found to be 4. The method was much more sensitive than the mercury salt method, the detection limit being about 1.5×10^{-9} mol l⁻¹. In this method, copper(II) was added in excess over the MBT in order to ensure that the maximum signal was obtained. The transition from accumulation of the mercury salt to accumulation of the copper(I) salt was studied at sub-stoichiometric concentrations of copper(II) relative to the MBT concentration and is illustrated in Fig. 1. The addition of increasing amounts of copper(II) to the voltammetric solution caused the mercury–MBT peak to decrease and the Cu–MBT peak to increase. The effect of accumulation potential at a sub-stoichiometric concentration of copper(II) is shown in Fig. 2. When the accumulation potential

was changed from +0.1 through +0.05 to 0 V, there was an increase in the size of the copper(I) peak relative to that of the mercury peak. The height of the copper(I) peak remained unchanged at low negative accumulation potentials whilst the mercury peak was eliminated. In the presence of excess of copper(II), the mercury peak was not formed at potentials more negative than +50 mV.

Typical cathodic stripping voltammograms obtained for the accumulation of the nickel(II) complex of MBT are shown in Fig. 3. These were obtained at pH 8.6 in Britton–Robinson buffer. The high sensitivity of this method is apparent. The sensitivity of the nickel method under these conditions is about ten times that the copper(I) method. Clearly, detection limits in CSV can be increased by increasing the accumulation time used. A comparison of the copper and nickel methods can be made by comparing the size of the peak currents at the 7×10^{-9} mol l⁻¹ MBT level for a 300 s accumulation, *viz.* 2.5 and 30 nA, respectively. Further results, which will be reported later, indicate that the sensitivity of the nickel method is dependent on buffer composition as well as pH, and that optimized procedures will give an even higher sensitivity.

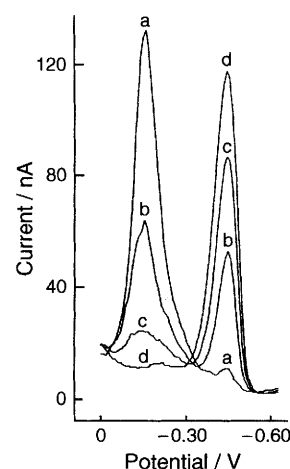


Fig. 1 Effect of sub-stoichiometric concentrations of copper(II) on the mercury–MBT CSV peak obtained in Britton–Robinson buffer of pH 4. Accumulation potential = 0 V. Accumulation time = 120 s. MBT concentration = 9.0×10^{-7} mol l⁻¹. Copper(II) concentration: a, 0; b, 0.8×10^{-7} ; c, 1.6×10^{-7} ; and d, 2.4×10^{-7} mol l⁻¹.

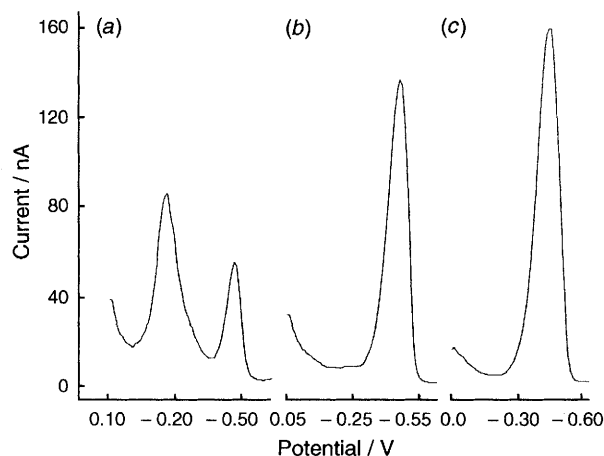


Fig. 2 Effect of accumulation potential on the mercury–MBT CSV peak obtained in Britton–Robinson buffer of pH 4 with a sub-stoichiometric concentration of copper(II). Accumulation potential: (a), +0.10; (b), +0.05; and (c), 0 V. Accumulation time = 120 s. MBT concentration = 9.0×10^{-7} mol l⁻¹. Copper(II) concentration = 7.9×10^{-7} mol l⁻¹.

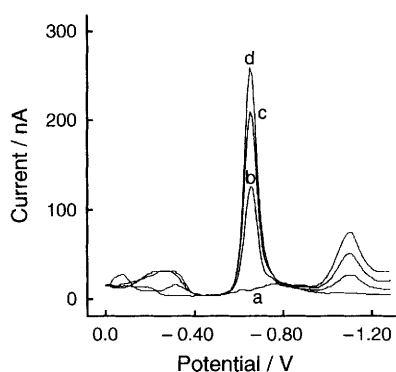


Fig. 3 Typical cathodic stripping voltammograms for nickel(II)-MBT obtained in the presence of different (excess) concentrations of nickel(II) in Britton-Robinson buffer of pH 8.6. Accumulation potential = 0 V. Accumulation time = 60 s. MBT concentration = 4.8×10^{-7} mol l $^{-1}$. Nickel(II) concentration: a, 0; b, 0.85; c, 1.7; and d, 2.55×10^{-4} mol l $^{-1}$.

Conclusions

This paper describes the CSV of MBT, which is part of a fuller study of a range of compounds comparing indirect CSV methods at a HMDE involving accumulation as mercury, copper(I) or nickel salts/complexes. Accumulation of mercury-MBT is effected optimally in Britton-Robinson buffer of pH 4 at 0 V versus Ag-AgCl (3 mol l $^{-1}$ KCl) and the reduction peak at -0.15 V is used for the determination. The detection limit is about 3×10^{-7} mol l $^{-1}$. Alternatively, MBT can be accumulated (also at pH 4) at -0.10 V in the presence of copper(II) as its copper(I) salt using the copper(I) reduction peak at -0.45 V for determination. The detection limit is about 1.5×10^{-9} mol l $^{-1}$. MBT forms stable complexes with nickel(II),

which can be accumulated most effectively at -0.4 V, in pH 8.6 buffer: determination is made using the catalytic nickel peak at -0.6 V. The nickel method is about ten times more sensitive than the copper(I) method and it will discriminate against non-complexing thiol interferents. The catalytic nature of the nickel peak for MBT seems to be more evident than with thiols, such as cysteine, studied so far by this method. Copper(II) interferes only slightly in the nickel method. Our experience is that the mercury salt accumulation method for the determination of MBT is not only less sensitive, but is also less reliable than the copper and nickel methods. This is being investigated further.

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