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# CATHODIC STRIPPING VOLTAMMETRY AND SENSORS : SULFONAMIDES AND THIOLS ¶

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## Introduction

Disposable sensor devices, such as those for glucose, use enzyme reactions in order to reach high sensitivities and low detection limits. The cathodic stripping voltammetric methods being developed in our laboratory are, in part, designed to be adapted for use in capillary-fill or similar disposable sensor devices [1,2]. If accumulation could be effected in a sensor device incorporating adequate convective mass transport this should allow uncatalysed reactions to reach sufficiently low detection limits for the purposes of trace analysis.

The first reported work on cathodic stripping voltammetry from our laboratory was carried out by A.A.Barros on synthetic food colouring matters [3] under an initial collaboration with Professor J.O.Cabral in Porto. New collaborative studies have started on the CSV and reduction mechanisms of nitroprusside with Professor J.Simao in Aveiro. Fogg made Ph.D. studies of the Boedeker reaction (nitroprusside + sulfite) [4-7] , the main finding being the important visible role played by ion pairing by alkali metal ions on this equilibrium. A preliminary paper was published on the CSV of nitroprusside in 1994 [8]. Preliminary work on the new studies in Aveiro are reported elsewhere in this journal.

Fogg has attempted recently to document systematically and fully the different methods that can be used to accumulate determinands in stripping voltammetry (SV) and the combinations of accumulation and stripping methods that can be used [9]. A preliminary paper has been published also on the nomenclature of SV and on a proposed acronym system [10]. This work is being undertaken towards the production of an IUPAC publication. In considering a general nomenclature some more recent and less well known

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methods of accumulation need to be considered [9,10]. Some chemical species are determined, in the presence of copper(II), as copper(I) complexes or salts [11]. Determinands can be accumulated in a reduced form, and can then be determined by further reduction [12]. Some determinands are reduced reversibly and their reduction products are also adsorbed on the HMDE. Because of this they can be determined by adsorption and reduction in the normal way, or they can be accumulated cathodically and then determined by reoxidation anodically [13,14]. Selenium(IV) can be accumulated as $Cu_2Se$, in which both selenium(IV) and copper(II) are reduced.[15] Some stripping methods, such as particular methods for tin(IV) [16] and arsenic [17], involve an intermediate electrochemical step, and others involve a change of electrolyte solution after accumulation [18]. The coupling of the reduction of a metal ion in an adsorbed metal complex with its chemical regeneration by a chemical oxidant in the solution gives rise to higher (catalytic) currents and lower detection limits [19]. There are many more variants of the electrochemical stripping analytical technique.

The main aim of this paper is to review our recent work on two aspects of CSV, namely the use of the addition of copper(II) and nickel(II) in determining suitable organic compounds indirectly. These techniques will be illustrated here using recently developed methods for the determination of sulfonamides and thiols. Cathodic stripping voltammetry at a hanging mercury drop electrode (HMDE) has been used extensively as a trace technique. Suitable organic compounds can be accumulated by adsorption on the HMDE and then determined by reduction [20]. Trace metals can be adsorbed as metal complexes and then can be determined directly, by reducing the metal ion, or indirectly, by reducing the ligand [21]. Organic compounds that are not reducible but which can complex metals can be determined indirectly in a similar way by adsorbing a metal complex and then reducing the metal ion. To date, however, only methods involving faradaic accumulation steps have been used for this purpose. In the original CSV method organic compounds such as thiols were accumulated as mercury (I or II) salts, mercury metal being oxidised at a less positive potential in the presence of the thiol: the mercury ion was reduced back to mercury metal in the determination step. In



the case of some organic compounds that can be determined in this way the potential window in which the mercury salt is produced is rather narrow and is close to the potential at which the bulk mercury is oxidised. In these and many other cases accumulation in the presence of copper(II) as copper(I) salts or complexes gives better results: accumulation of copper(I) salts or complexes by those compounds that form them is usually effected at around -0.1V vs SCE. A large increase in accumulation at or near this potential is a good indication that a copper(I) salt or complex is being accumulated rather than a copper(II) complex [9] : again, in the case of the formation of insoluble salts, the fact that only the copper salt , and not insoluble salts of other metal ions such as lead, zinc or cadmium, is accumulated, suggests that it is the copper(I) salt that is being accumulated. In these laboratories methods of accumulating and determining the tripeptides GGH and GHG as copper(I) complexes have been developed [22,23]. As the organic compound is released when the mercury or copper(I) ions are reduced these methods are potentially catalytic.

The catalytic nickel wave has been well-studied in polarography, but was not used analytically as the Brdicka wave was more sensitive. Its use in CSV, however, has been shown in our laboratories to be advantageous in terms of increased selectivity, and this use of added nickel(II) in CSV is described below.

Sulfonamides.

Bult has reviewed the use of metal complexes of sulfonamides in pharmaceutical analysis and in drug therapy [24]. Sulfonamide drugs are soluble in both acidic and alkaline solution owing to the presence in their structures of the aromatic amine and the sulfonamide groups, respectively. Many sulfonamide drugs are prescribed as salts, the acidic hydrogen in the sulfonamide group being displaced to give a water soluble drug. In forming metal complexes this acidic hydrogen is lost in competition with the metal ion allowing the sulfonamide nitrogen to serve as a donor atom in the complex. Stable complexes are reported to be formed, however, only by those sulfonamides whose structures contain a heterocyclic nitrogen atom ortho to the sulfonamide group. Bult and coworkers [25] prepared and studied a range of copper(II)-sulfonamide complexes. Sulfadiazine, sulfamerazine,

sulfamethoxydiazine, sulfamethoxypyridazine, sulfapyridine and sulfathiazole were shown to form dimeric complexes of the type $Cu_2L_4$, in which the sulfonamide and the heterocyclic nitrogen atoms in each sulfonamide molecule are coordinated to two different copper ions. A bidentate, mononuclear complex would have four-membered rings. Sulfonamides with a substituent on the other carbon atom in the heterocyclic ring that is ortho to the heterocyclic nitrogen atom, eg. sulfadimethoxine, sulfadimidine and sulfasomidine, on the other hand, gave complexes classified as monomeric or polymeric. This modified behaviour was reported to be caused by steric hindrance by this substituent.

Argentimetric methods have been reported for the determination of those sulfonamides which form insoluble silver salts, in general those that form stable copper complexes [24,26]. The characteristic colours given by individual sulfonamide drugs in the presence of copper(II) are used as identity tests [27].

Thus, previous workers have shown that many sulphonamides form stable copper(II) complexes[24,25]. Work in our laboratories has shown that those sulfonamides that form stable copper(II) complexes can be accumulated as (stable) copper(I) complexes at an HMDE, and can then be determined by cathodic stripping voltammetry [28]. Thus, sulfamerazine, sulfadimidine and sulfathiazole, for example, can be accumulated and determined indirectly by reduction of the complexed copper(I) to copper amalgam, whereas sulfanilamide, sulfaguanidine and sulfacetamide are not accumulated.

Determinations are usually made in pH 7 Britton Robinson buffer, but if a pH 6 EDTA buffer is used the CSV peak is eliminated completely. This use of EDTA buffer allows directly reducible sulfonamides, such as sulfasalazine, to be determined in the presence of non-reducible complexing sulfonamides even when copper(II) is present in the solution [29]. Because sulfasalazine forms copper(II) and copper(I) complexes its accumulation was expected to be modified in the presence of copper(II), but this proved not to be the case, probably because the signal due to the adsorption of the free sulfasalazine is so much larger than the copper(I) signals obtained with complexing



sulfonamides.

On the other hand, the CSV signal of another reducible and complexing sulfonamide, sulfachloropyridazine, is enhanced about four-fold in the presence of copper(II) [30]. This illustrates the potential interference of copper(II) in the direct determination of some complexing molecules. This interference can be overcome by the addition of excess of copper(II) or by using an EDTA buffer. The lack of enhancement of the signal in the presence of copper(II) when accumulation is carried out on open circuit shows the faradaic nature of the accumulation mechanism. Care should be taken, however, in interpreting open circuit CSV experiments, as the free ligand may well be accumulated to a different extent at the open circuit potential than at the closed circuit potentials usually used. This seems to be the case with sulfaquinoxaline for which preliminary results have shown that the open circuit signal is much lower than those at closed circuit potentials around 0V (unpublished work).

Thiols. The polarographic use of the catalytic nickel wave was not important analytically, because the catalytic hydrogen (Brdicka) wave obtained with nickel(II), and even more so with cobalt(II), was much more sensitive [31,32]. Banica has introduced the use of the catalytic nickel peak in CSV whilst working in our group [33-36]. The catalytic nickel peak is produced by the reduction of nickel(II) at a reduced overpotential: this occurs when the nickel(II) is complexed. Thiols are normally accumulated as mercury salts, mercury in the electrode being oxidised anodically in the presence of the thiol. In the case of cysteine and penicillamine, this peak at -0.4V is replaced in the presence of nickel(II) by the catalytic peak at -0.6V (pH 7) [33,36]. Glutathione, which forms a less stable nickel complex, also gives the catalytic nickel peak but the mercury thiol peak at -0.4V is only slightly diminished [34]. N-acetylcysteine is not complexed by nickel and the mercury thiol peak remains unchanged and no catalytic peak is observed [33].

Thus, thiols that form stable $Ni^{2+}$ complexes can be determined more selectively by adding $Ni^{2+}$. Furthermore, these thiols are masked by $Ni^{2+}$, allowing the peak at -0.4V to be used for the determination of non-complexing thiols.

In pH 7 phosphate buffer cysteine and penicillamine can be accumulated very efficiently at potentials between 0 and -0.4V and in this buffer are clearly accumulated mainly as their nickel complexes and not as their mercury salts. In pH 7 MOPS buffer, however, the extent of the accumulation falls off increasingly between 0 and -0.4V, and is virtually zero at -0.4V. Clearly accumulation in pH 7 MOPS buffer is as the mercury salt.

Although in theory the new nickel peak is catalytic in nature - because thiol is released to complex further nickel ion - as well as occurring at a reduced overpotential, the size of the current is still comparable with those of the mercury or copper(I) peaks. This indicates that the rate of nickel complex formation is comparatively slow.

Cystine and oxidised glutathione accumulate as their thiol reduction products. This is believed to be due to a chemical hydrolytic disproportionation reaction occurring on the electrode surface, rather than by direct reduction of the oxidised thiols, which would not be expected to occur at these potentials.

Our most recent studies on thiols have been with 2-mercaptobenzthiazole (MBT) (unpublished work). This thiol can be determined as its mercury, copper(I) and nickel(II) salts/complexes. Preliminary results indicate that a very large catalytic nickel peak is obtained, indicating that, in the case of MBT, complex formation with nickel is rapid, and a marked catalytic enhancement is obtained.

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# DIFFUSION AND THERMAL DIFFUSION IN ELECTROLYTE SOLUTIONS ¶

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## 1. Introduction

Isothermal and thermal diffusion in electrolyte solutions are transport properties that may give important clues to the understanding of the complex structure of those electrolyte solutions. Furthermore, and once diffusion is a very common phenomenon, experimental data on diffusion coefficients D are in high demand, both from industrial areas and from other scientific fields. In fact, not only the availability of these data is very scarce, [1], but their accurate experimental measurement has been so difficult that only a few researchers in this century have managed to obtain diffusion coefficients with reasonable accuracy. Harned's [2] conductimetric technique, Miller's [3] optical system and our open-ended capillary cell have provided reliable data on D. Harned's and Miller's methods are experimentally very difficult to operate and the former is only good for dilute solutions, whereas the latter, being an optical method, only works for relatively concentrated solutions. Our system is operationally much simpler than any of the above and has successfully been used with solutions more diluted than possible with Harned's cell and also with reasonably concentrated solutions. It has been possible to have a precision similar to that of the highly precise Harned method and, we believe, also equally accurate [4]. It has been successfully used in a range of concentrations from 0.001 M (and sometimes lower) to 0.1 M and higher in aqueous solutions of the following electrolytes: HCl [5]; $KClO_4$ [6]; KCl with sucrose [7]; $CdCl_2$ [8]; $CdSO_4$ [9]; $NiCl_2$ [10]; $Al(NO_3)_3$ [11]; $Ca(NO_3)_2$ [12]; $Ba(ClO_4)_2$ [13]; $BaBr_2$ [14]; KSCN [15]; $Mg(NO_3)_2$ [16]; $MgSO_4$ [17]; $BeSO_4$ [18]; $CoCl_2$ [19]; $NH_4VO_3$ [20]; $LiClO_4$; $NaCH_3COO$; $MnCl_2$; $CuCl_2$; CsI; $Ba(ClO_4)_2$; $CdI_2$; $Cd(NO_3)_2$; $BaBr_2$; $CdI_2$; $CdBr_2$; $AlCl_3$; $MnSO_4$. It has also been adapted to measure diffusion coefficients of electrolytes imbibed in polymers [21-24], and, to study diffusion in solutions subjected to magnetic fields [25].

The cell was initially developed for measurements of Soret coefficients by thermal diffusion, using the initial rate procedure, that is the rate of the initial ion migration in a solution where a temperature gradient is suddenly applied. In fact, such a procedure requires the knowledge of the isothermal diffusion coefficient D. Soret coefficients, and consequently heats of transport,

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