

O₂-meter. All measurements were done in a 0.1M phosphate buffer solution of pH=6.87.

In Fig.1 are shown calibration curves of the enzyme sensor, which show good linearity for concentrations from 10⁻⁵M to 3.10⁻³M, and good lifetime of one month. The difference in initial response and response after 15 days is small. The sensor is very precise and can be applied to non coloured solutions, thus having an advantage over the colorimetric method [3].

Response times are shown in Fig.2 for different concentrations together with the corresponding calibration plot. The final potential is reached within less than a minute, and does not alter with time.

This catalase sensor is quite robust and portable enabling its use for measuring hydrogen peroxide *in situ*. The quantity of sample used is very small. Comparing with the methods normally used for hydrogen peroxide determination the electrochemical method seems a very reliable one.

In conclusion, this enzyme sensor responds linearly to hydrogen peroxide over a wide concentration range, has a good detection limit, a very short response time and a reasonable lifetime for the immobilised enzyme.

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STRIPPING VOLTAMMETRY AT HYDRODYNAMIC MERCURY THIN FILM ELECTRODES

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In anodic stripping voltammetry from mercury electrodes, mercury thin film electrodes (MTFE) offer advantages over hanging mercury drop electrodes (HMDE), in that the current peak in redissolution is narrower and the peak current higher, offering improved sensitivity, detection limits and reproducibility. Glassy carbon substrates are generally used, and pre-deposition or co-deposition of mercury with the metal ion successfully employed. An important advantage of the MTFE is that it is directly usable in forced convection systems with electrode movement or solution flow, thus being applicable to on-line electroanalysis. Additionally, at positive potentials the bare glassy carbon electrode can be used for other electrode reactions, since the mercury is readily removed electrochemically or mechanically.

Conventionally, although the pre-concentration (or deposition) step is carried out with forced convection, this is stopped during stripping, ostensibly to give better reproducibility. The increasing use of electrochemical detectors in flow systems, particularly on-line, makes it desirable to continue solution flow. We have therefore re-examined the question with respect to linear scan stripping, theoretically and experimentally, at the rotating disc electrode (uniformly accessible and with electrode movement) and at the wall-jet

disc electrode (non-uniformly accessible and with moving solution) as typifying the various experimental conditions that can arise. Reversible electrode kinetics are assumed.

The models used for deriving the theoretical shape of the redissolution peaks at very thin MTFE's are shown in Fig.1. Stripping

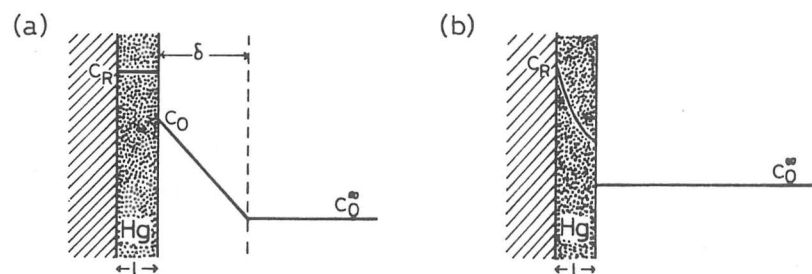


Fig.1 Models for (a) convective and (b) non-convective stripping from MTFE; C_0 concentration of metal ion in solution and C_R concentration of metal in mercury.

in stationary solution assumes a parabolic concentration profile in the mercury film and constant solution concentration of metal ions at all points [1]; the fairly symmetric peak agrees well with experiment. Convective stripping [2,3] results in a narrower, asymmetrical peak, calculated assuming no concentration gradient in the mercury film and a linear concentration gradient in the diffusion layer perpendicular to the electrode surface. In terms of the dimensionless sweep rate σ ($=nF/RT$) ν) the current peaks can be expressed in both cases by

$$i = Z(\sigma t)nFA\sigma C_R l$$

where C_R is the concentration of metal in the mercury before stripping begins and $Z(\sigma t)$ a current function whose maximum value is 0.298 (non-convective) and 0.368 (convective). Fig.2 shows the shape of the current peaks and in Table 1 the expected half widths ($nb_{1/2}$) and peak

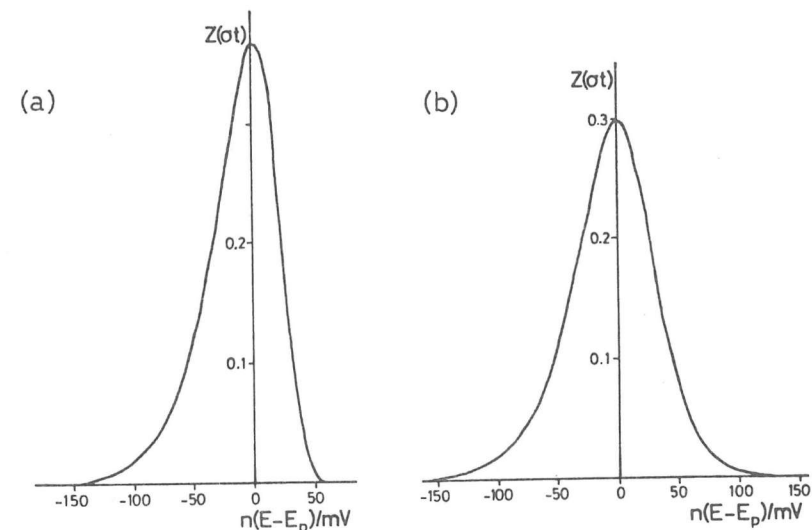


Fig.2 Theoretical peak shape for (a) convective, and (b) non-convective stripping from MTFE. $Z(\sigma t)$ is dimensionless current function and E_p peak potential (see text).

Table 1. Parameters describing the redissolution current peaks

	Convective stripping	Non-convective stripping
i_p	$0.368nFA\sigma C_R l$	$0.298nFA\sigma C_R l$
$nb_{1/2}/mV$	62.8	75.5
$n(E_p - E^{0'})/mV$	$\frac{RT}{F} \log \left(\frac{\delta l \sigma}{D_0} \right)$	$-1.43 + \frac{RT}{F} \log \left(\frac{l \sigma^{1/2}}{D_0^{1/2}} \right)$

positions are given. The narrower convective stripping peaks and their lack of symmetry can bring important advantages to peak resolution in mixtures.

The wave shape and position for convective stripping were studied experimentally using solutions of Pb(II) with preformed mercury films in KNO_3/HNO_3 electrolyte [3]. The assumption of zero concentration

gradient within the mercury film limits the maximum scan rate to around 20mV s^{-1} . Good reproducibility was found with experiments at the rotating disc and at the wall-jet disc electrode. At the former excellent agreement was found between experiment and theory at a variety of rotation speeds and scan rates. However, at the wall-jet electrode, broader peaks were found except at very high flow rates ($>0.125\text{ cm}^3\text{ s}^{-1}$) and low scan rate, although the asymmetric wave shape typical of convective stripping was still apparent. Two factors can be invoked to explain the differences, reflecting the non-applicability of assumptions in the model at the wall-jet:

(i) The non-uniform accessibility implies the possibility of different electrode kinetic regimes over the electrode surface. This will be more accentuated the lower the flow-rate.

(ii) Diffusion parallel to the electrode surface is significant at low flow rates, since radial convection is low.

Despite the broader peaks at the wall-jet electrode advantages in peak resolution, due to peak asymmetry, and the good reproducibility are to be gained from convective stripping. This is important for the on-line use of these electrodes.

Similar considerations can be applied to tubular and channel electrodes, which are more uniformly accessible than the wall-jet electrode.

References

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THE GLASSY CARBON ELECTRODE/TETRABUTYLAMMONIUM ELECTROLYTE SOLUTION INTERFACE IN *N,N*-DIMETHYLFORMAMIDE SOLVENT

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Carbon electrodes have the advantage of being usable over a wide potential range in a variety of solvents, that has made their application widespread. However, owing to the existence of surface groups on the carbon, they cannot be regarded as inert, which is often manifested by significant background currents.

Studies previously undertaken by ourselves using glassy carbon (GC) electrodes in tetraalkylammonium electrolytes in *N,N*-dimethylformamide (DMF) [1] have shown the large background currents obtained in supporting electrolyte only at negative applied potentials. Additionally, cyclic voltammograms show variation with the anion and, as shown in Fig.1, small peaks can appear, in this case for chloride anion at -0.7V .

In this work the glassy carbon electrode/tetrabutylammonium (TBA) electrolyte interface in DMF was further studied for perchlorate (TEAP), bromide (TBAB) and chloride (TBAC) salts at varying concentrations from 0.01M to 0.20M and over the potential range 0.0 to -2.0V vs SCE. The structure of the interface was probed using the ac impedance technique with a Solartron 1250 Frequency Response Analyser coupled to a 1286 Electrochemical Interface and HP9816 computer. A sinusoidal perturbation of 5mV rms was superimposed on top of the dc