RAPID SCANNING VOLTAMMETRY UNDER STEADY-STATE CONDITIONS IN A FLOW THROUGH THIN LAYER CELL WITH A MICROELECTRODE

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

A microelectrode based detector system has been developed for measurement of steady state voltammetric curves in flowing solutions. Two microprocessors operating in parallel allow the direct transfer of collected data to a floppy diskette. Long term experiments can then be performed, with individual voltammograms being rapidly obtained, recorded and stored. The system can be used with scan rates up to 10 $V s^{-1}$ and with 1 mV resolution over a potential range of 2·5 V. When a 10 μm diameter micro-disk platinum electrode serves as the working electrode, rapid scan voltammetry (scan rate 1 to 10 $V s^{-1}$) can be undertaken under steady state conditions for reversible processes with a flow rate in the range of 1 to 3 ml min^{-1} as evidenced by the observation of sigmoidal rather than the peak shaped curves obtained with previously described rapid scan systems. That is, complete voltammograms can be obtained with minimal distortion due to uncompensated resistance and charging current which is not the case when conventionally sized electrodes are used or when microelectrodes are used at excessively high scan rates where linear diffusion terms become important. The working microelectrodes were developed to suit a conventional thin-layer cell design and therefore permit ready adaptation to existing flow through electrochemical detection systems. The detection limits for the determination of ferrocene in methanol at flow rates up to 3 ml min^{-1} were 10^{-6} mol . . dm^{-3} after background correction, and the response was found to be linear over the concentration range 10^{-3} to 10^{-6} mol dm^{-3}. Three-dimensional methods of data treatment and contour plots can be used to interpret results obtained from steady state or near steady state voltammograms of incompletely resolved chromatograms as demonstrated with a range of biologically important compounds.

Rapid scanning electrochemical detectors, capable of performing linear sweep or cyclic voltammetry in flowing solutions, have allowed on line characterization of electroactive species (see refs[1-15] for example). As with the diode array spectrophotometer, where the complete spectrum is obtained, rather than data at a single wavelength, the differentiation of chromatographically unresolved species having different half-wave potential is possible when the entire current-voltage curve is

recorded instead of the current at a fixed potential[15]. However, while the recent development of electrochemical detectors capable of recording the entire experiment has added specificity to the analysis, unlike its spectrophotometer equivalent, the rapid scanning required introduces limitations because of the increasing importance of linear diffusion and charging current[16,17], relative to the sensitive steady-state response obtained at constant potential (zero scan rate).

The scanning electrochemical detectors available have been developed with a variety of working electrodes ranging from conventional disk sized electrodes[1,2] to a carbon fibre microelectrode[1,3-8]. Because of the electrode geometry and size of electrodes employed or mechanism of the electrode process, the current–potential (i–E) curves obtained in these studies were usually not recorded under steady-state conditions so that lower sensitivity, increased ohmic iR drop and non-faradaic currents present considerable difficulty at scan rates above 200 mV s^{-1} relative to constant potential (zero scan rate experiments). Attempts to overcome some of these problems by replacing the linear sweep with various techniques such as differential pulse and square wave voltammetry[3,7,9,10,14,18,19], have achieved mixed success and have been best utilised when coupled with micro-fibre electrode technology[3,7,14].

Recently micro-disk electrodes have become popular in electroanalytical chemistry and have been successfully used as constant potential detectors in flowing solutions (flow injection analysis and liquid chromatography)[1,20-25]. This micro-disk electrode methodology would benefit from the rapid scan method more than most other classes of electrode because if the electrodes are sufficiently small then radial rather than linear diffusion predominates and steady-state i–E curves are obtained even with relatively fast scan rates. The use of a flowing solution also contributes to the attainment of the steady state[24].

The i–E curve obtained under steady-state conditions is sigmoidal shaped rather than the traditional peak shape because of the enhanced mass transport to and from the working electrode surface[24,26]. The increase in current density at the electrode surface should not only improve the sensitivity of the system (as measured by the faradaic-to-charging current ratio) but also minimise the effect of iR drop on the system[16,25,26]. Under steady state conditions, the iR drop may be reduced to a level where the system is able to tolerate samples of low ionic strength and allow a two electrode system to be used, eliminating the need for a potentiostat[27-31]. Because of the smaller surface area of the working electrode there is also a reduction in the double layer capacitance of the cell resulting in smaller time constants. The smaller time constant allows faster scan rates to be achieved with microelectrodes thereby enabling the mechanistic study of very fast electrochemical reactions (see refs[27-31] for example). However, in the studies at fast scan rates described to date in flowing solutions the scan rates used have been so fast that linear diffusion terms are dominant and responses are not obtained under steady state conditions.

The disadvantages of micro-disk electrodes are associated with noise problems in measuring the small electrolysis currents that result from use of small electrode areas. The problem is compounded by the fact that the signal is so small that the noise obtained may not solely originate from the cell but could be derived from any accompanying circuitry (e.g.: potentiostat) or external sources (e.g.: computers, power supply, etc.). The level of current can be improved with arrays of micro-disk electrodes or micro-strip electrodes[25,32] or by the use of a current multiplier to enhance the signal prior to leaving the protection of the Faraday cage[33].

This paper describes the development of a micro-disk electrode based detector capable of rapid scanning voltammetry in flowing solutions under steady-state conditions. That is, conditions of scan rate, flow rate and mechanism have been chosen so that a sigmoidal shaped curve is obtained for a reversible process rather than a peak shaped curve as obtained in previous studies. The speed with which the detector must scan the potential to record the *i–E* curve in a flowing solution requires that the detector be computer controlled. If the one computer is used, the data that is collected must be stored in random access memory (RAM), until completion of the experiment. With most personal computers, this severely restricts the number of scans which can be collected or the number of data samples which can be taken per scan. The detector described in this paper uses two personal computers processing information independently (in parallel) and thus enabling any collected data to be stored directly to a floppy diskette. This allows the detector to be run indefinitely with no restrictions on the number of scans that can be collected during the experiment. The transfer of data between the two computers restricts the system to at least a 1·5 second delay between scans which is sufficiently small to allow at least ten scans to be collected to represent a normal chromatographic peak. The parallel processing also allows one processor to be devoted to running the cell enabling scans to be performed with 1 mV resolution at scan rates up to $10\ V\ s^{-1}$.

The detector has been designed to utilise as much commercially available flow through cell equipment as possible. For this reason the microelectrodes were constructed to directly fit into a commercially available thin-layer cell design which enables the detector to be used on many previously developed chromatographic or flow injection assays employing electrochemical detection at conventionally sized electrodes.

EXPERIMENTAL

Chemicals

The mobile phase for use in chromatography experiments consisted of a mixture of 0·1M aqueous phosphate buffer pH 3·5 and methanol containing 0·1M tetraethylammonium perchlorate.

Sample solutions were prepared directly in the appropriate mobile phase. Ferrocene (Fischer Scientific Co.) and tetraethylammonium perchlorate were of electrochemical grade. Methanol was HPLC grade (Mallinkrodt). Phosphoric acid was purchased from Fischer Scientific Co. All other chemicals were obtained from Sigma Chemical Co., and high purity water was obtained from a Milli Q system. Fresh solutions were made for each series of experiments.

Apparatus

Wave form generation and data acquisition were performed with the combination of an Apple II plus (1·023 MHz) and a Motorola 6809 (1·8 MHz) processor based custom built computer. The 6809 based system was equipped with a 12-bit analog-to-digital converter (A/D) (ADC HS12BMC) and a 16-bit digital-to-analog converter (D/A) (DAC 71COB-V). The D/A had a full output voltage range of −15 to +15 V, full scale. Each of the converters are protected with isolation amplifiers (AD625). The D/A was connected via a 1 : 5 voltage divider to an operational amplifier (OP-27) in a "voltage follower" configuration, with the output of the amplifier connected to the auxiliary electrode and the negative input connected to the reference electrode to control the cell potential. A cascade of amplifiers consisting of a current multiplier located in the Faraday cage and current-to-voltage converter located outside the Faraday cage connecting the working electrode to the A/D. The current mutliplier consisted of a 515K amplifier with a selectable 1 or 10Mohm feedback resistor in series with an OP-27 operational amplifier[33]. The current-to-voltage converter consisted of two OP-27 operational amplifiers in series with selectable gain. All leads were shielded, and components including the current-amplifier and current-to-voltage converter housing were grounded to the Faraday cage. All electronics associated with the cell were constructed with a 100 microsecond time constant. A triangular waveform was used in which the voltage was stepped in 1 to 10 mV increments. Cycling of the potential was commenced at some defined interval after injection of the sample (usually 4 s) and continued until the run was complete. Data was collected at every potential step and for every scan. Data are transferred between the two computers in 20K lots via a custom built parallel interface (constructed with 6121 parallel interface adapters)[34,35]. The process may take up to 1·4 s which is fast enough to enable transfer of data to occur between scans. Once collected by the Apple computer the data is stored on magnetic disk, meanwhile the 6809 continues to drive the electrochemical cell. All post-run processing was done in compiled BASIC or compiled FORTRAN on either a VAX 11/750 or NEC APC IV computer. Three dimensional plotting was performed with SURFER (Golden Software, Inc.). Data presented on figures were recorded with a digital plotter.

The chromatography system consisted of a 25 cm × 3·1 mm i.d. 5 μm octadecylsilane reversed phase column (Zorbax,Du-Pont Co.) with a 0·1M phosphate buffer (pH 3·5)–methanol (90 : 10) as the mobile phase. A Waters Model 510 HPLC pump was used to maintain a flow rate of 1·0 ml min^{-1}. All mobile phases were filtered through a 0·45 μm membrane filter (Millipore) and degassed under vacuum. The concentrations of adrenaline, 6-hydroxydopa, dopamine, dopa and tyrosine were 0·84, 0·83, 1·03, 1·08 and 0·97 . 10^{-3} mol dm^{-3}, respectively. The exact concentration of 6-hydroxydopa was unknown because of its instability in the mobile phase. A 50 μl of the sample mixture was injected onto the top of the column. The non-aqueous work for oxidation of ferrocene in methanol was performed at flow rates over the range of 0 to 3 ml . . min^{-1} with a 1 m × 0·5 mm i.d. teflon mixing coil replacing the column.

Electrochemical Cell and Electrodes

The electrochemical cell was of a Bioanalytical Systems, BAS, (TL-4) thin-layer design. The

auxiliary electrode was a 5 cm × 5 cm stainless steel block (BAS). The reference electrodes were Ag/AgCl (BAS RE-3 or RE-4). Platinum working electrodes of micro-dimensions were custom built. First the electrode material, platinum wire, obtained from Goodfellows Metals was attached to a supporting copper wire with a silver epoxy. The wire was then placed in a soda glass tube and the glass sealed around the platinum wire with a bunsen burner flame. The glass was then cut and polished to a cylindrical shape and sealed with Torr seal (Varian) in a perspex block cut to fit the BAS thin-layer cell. Finally, the working surface of the electrode was cut and polished initially with wet and dry emery-paper and then alumina slurry to give a mirror finish. The diameter of the micro-disk electrode very closely approximates that of the platinum wire.

RESULTS AND DISCUSSION

Oxidation of Ferrocene under Conditions of Flow Injection Analysis

Studies to evaluate the detector performance were undertaken on the reversible oxidation of ferrocene[36] in methanol (0·1M Et_4NClO_4) at 25°C in the thin layer cell in the flow injection analysis mode (i.e. no chromatographic column was present) and on stationary solutions (zero flow rate).

Effect of Electrode Size

Voltammograms for oxidation of 10^{-3}M ferrocene with platinum disk electrodes, ranging from 500 μm to 10 μm in diameter, obtained in both static and flowing solutions, were studied in methanol to establish a suitable working electrode size in a thin layer cell to retain a steady state response in the presence of flowing solutions. The voltammograms obtained on stationary solutions at a scan rate of 100 mV . . s^{-1} with a 10 μm diameter electrode demonstrate a close approximation to the steady-state response via observation of an almost sigmoidal shape. The $(E_{1/4} - E_{3/4})$ value of (60 ± 5) mV is close to the theoretical value of 56 mV expected for a steady state reversible one electron oxidation process at 25°C (ref.[24]). As the size of the electrode increases, linear diffusion terms increase in importance and the response deviates from steady-state behavior as evidenced by the appearance of a peak shape (Fig. 1). The ohmic *iR* distortion also increases with the advent of linear diffusion (Fig. 1). Thus, the peak-to-peak separation of 250 mV with the 500 μm electrode, because of *iR* drop, is well in excess of the reversible value of 56 mV expected theoretically for linear diffusion. Steady-state conditions are important to minimise the *iR* drop[37,38].

Effect of Flow Rate and Scan Rate

Both flow rate and scan rate as well as electrode size and the mechanism for the oxidation or reduction process may influence the shape of voltammograms obtained in flowing solutions[8]. Figure 2 shows voltammograms of ferrocene recorded with

increasing flow rate conditions in a thin layer cell and with a 10 μm electrode. The effect of increasing the flow rate is to increase the limiting current and at the same time assist in the attainment of completely steady state behavior which is desirable from the point of view of achieving the optimal faradaic to charging current response and to minimising *iR* drop[24,37,38]. The steady state corresponds to overlap of forward and reverse scans in the cyclic voltammetric experiment and to removal of the peak originating from the presence of linear diffusion. The near steady state response with no flow is characterised by a small separation in the forward and reverse scan directions[39]. Data in Fig. 2 can be compared with data in Fig. 1 to

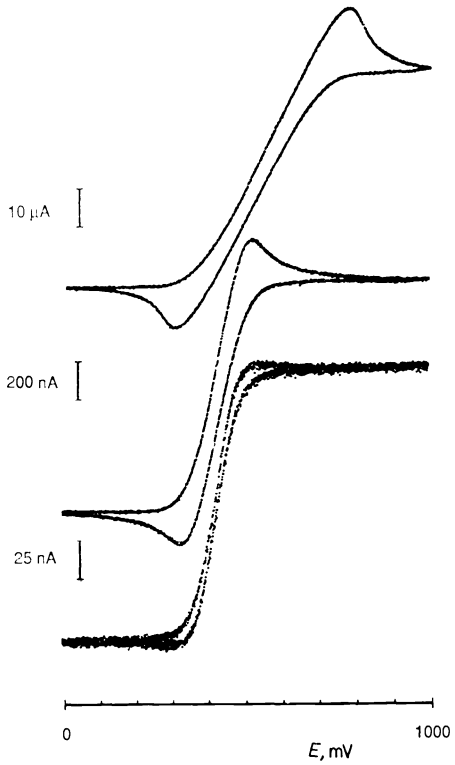

FIG. 1

Cyclic voltammograms obtained at a scan rate of 100 mV s^{-1} in a thin layer cell for static solutions of 10^{-3}M ferrocene in methanol (0·1M Et_4NClO_4). Platinum electrodes of diameter 500 μm (top curve), 50 μm (middle curve) and 10 μm (bottom curve) were used

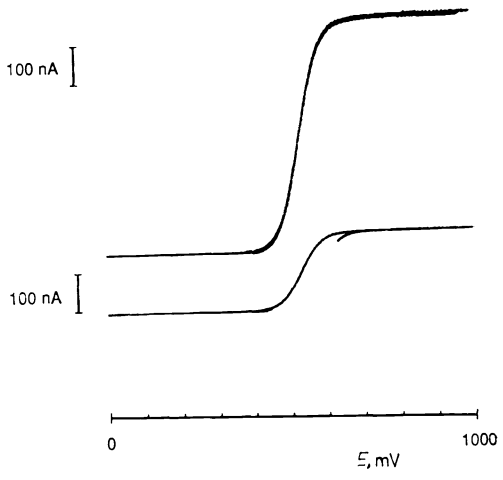

FIG. 2

Cyclic voltammograms of 10^{-3}M ferrocene obtained at a scan rate of 100 mV s^{-1} in a thin layer cell in methanol (0·1M Et_4NClO_4) under both slow (0·1 ml min^{-1}) (bottom curve) and fast (3·0 ml min^{-1}) flowing (top curve) conditions with a 10 μm diameter platinum disk electrode

demonstrate a change in wave shape and minimisation of the *iR* drop problem occurs as the steady state response is achieved at high flow rates. In the presence of a flow rate of 3·0 ml min^{-1}, the forward and reverse responses are equivalent. The wave shape is now the theoretically expected one for a reversible steady state voltammogram[24,26,39] and corresponds to the minimal *iR* drop situation[37,38].

The effect of scan rate on voltammograms for oxidation of ferrocene with a flow rate was 1·0 ml min^{-1} and at a 10 μm platinum working electrode are shown in Fig. 3. At slow scan rates (100 mV s^{-1}), the steady-state response is observed but as the scan rate is increased to 10 V s^{-1} the presence of linear diffusion is evidenced by the increasing separation observed between the forward and reverse scans. However, even with a scan rate as fast as 10 V s^{-1}, the near steady state response is achieved[22]. This result implies that little change in analytical sensitivity or *iR* drop problems will be observed at a fast scan rate, relative to slow scan rate as departures from steady state are minimal. In contrast when linear diffusion terms are dominant at fast scan rate, peak to peak separations in cyclic voltammograms are commonly 200 mV or greater as is the case in one of the curves in Fig. 1.

Linearity and Sensitivity with Background Subtraction

Direct measurement of voltammograms obtained with low concentrations of ferrocene in methanol at a platinum electrode is complicated because the faradaic signal is superimposed upon an overlapping background current response resulting from a platinum oxide formation process[40,41]. Interaction of the platinum oxide layer[40,41] with methanol leads to the small response over the range of 0·5 to 0·8 V vs Ag/AgCl which overlaps with the ferrocene oxidation process. This small background response is followed by the major solvent oxidation response which occurs at more positive potentials (Fig. 4*a*).

However, provided the background signal is reproducible it can be subtracted from the steady state voltammogram as is the case with a non steady state response[4]. After the initial settling period of up to 5 scans, the background current at microelectrodes in a thin layer cell was found to be very reproducible under flowing solution conditions in methanol. Background subtraction was performed by first averaging a representative set of background scans (usually five) to give a background voltammogram, then subtracting this background voltammogram from the voltammogram of interest. Figure 4*a* shows the voltammogram of 2 . 10^{-6}M ferrocene before background subtraction and the background obtained at a flow rate of 1·0 ml min^{-1} and a scan rate of 1 V s^{-1} in the thin layer cell. The similarity of the ferrocene and background responses is readily apparent from this figure. Figure 4*b* shows the voltammogram for oxidation of 2 . 10^{-6}M ferrocene after background subtraction. A signal to noise ratio of 3 : 1 was achieved under the conditions of Fig. 4, although the lack of a perfectly sigmoidal shaped curve shows

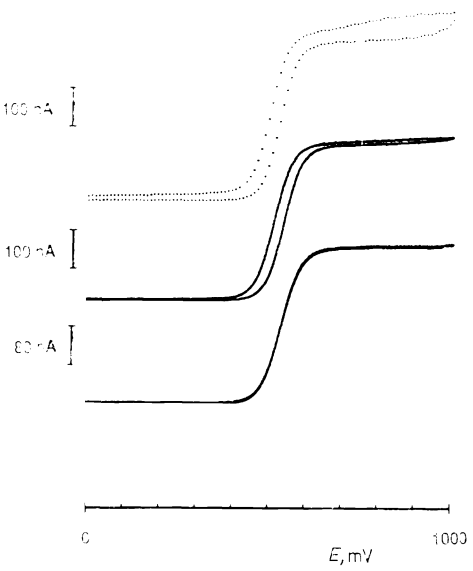

FIG. 3

Cyclic voltammograms for oxidation of 10^{-3}M ferrocene in methanol (0·1M Et_4NClO_4) at scan rates of 100 mV s^{-1} (bottom curve), 1 V s^{-1} (middle curve) and 10 V s^{-1} (top curve) with a 10 μm diameter platinum disk electrode in a thin layer cell. A flow rate of 1·0 ml min^{-1} was used

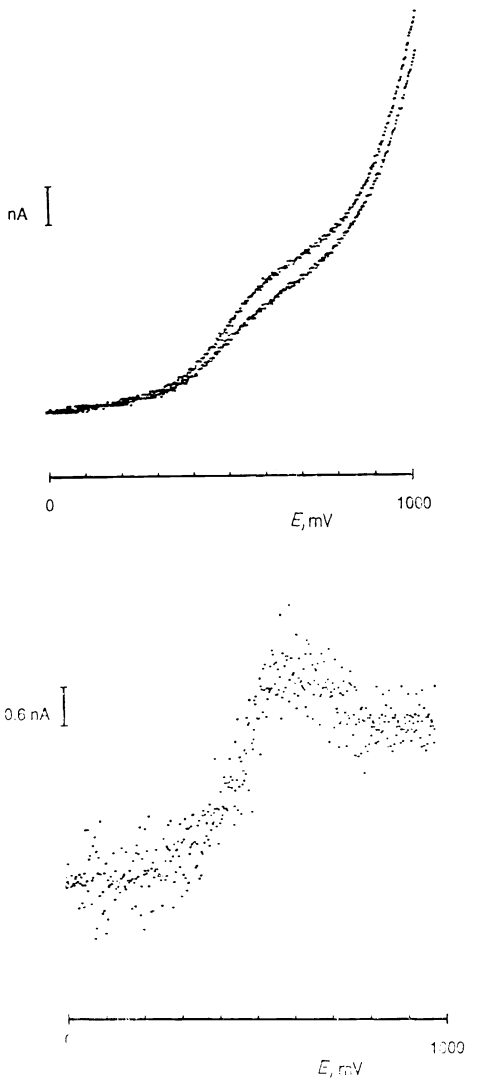

FIG. 4

Linear sweep voltammograms obtained in methanol (0·1M Et_4NClO_4) of *a* 2 . 10^{-6}M ferrocene (top curve) and background (bottom curve); *b* 2 . 10^{-6}M ferrocene after background subtraction. The signal to noise ratio is 3 : 1. A flow rate of 1·0 ml min^{-1} and a scan rate of 1 V s^{-1} was used in these experiments with a thin layer cell having a 10 μm diameter platinum disk electrode

that the subtraction contains a small systematic error. Detection limits in methanol for the determination of ferrocene could be improved either by reducing the level of background current (e.g. choosing a carbon rather than platinum working electrode surface) and by increasing the dynamic range of the detector (presently limited to 4 095). A log-log plot of the limiting current obtained at 0·7 V vs Ag/AgCl versus concentration of ferrocene revealed that the detector system displays linearity over the ferrocene concentration range of 10^{-6} to 10^{-3} mol dm^{-3} (the correlation coefficient and slope 0·9986 and 0·9334, respectively) using a platinum 10 μm diameter microelectrode in a thin layer cell under steady state conditions with a flow rate of 1 ml min^{-1}. The advantages of high speed, excellent sensitivity and minimal *iR* drop can therefore be achieved at a microelectrode disk of this size under flowing solution conditions. A multichannel microelectrode electrochemical detection system[42] also achieves steady state detection and similar performance to that described in this paper, although it is a much more complex method from the point of view of electrode construction and maintenance.

Detection of Biologically Important Compounds under Chromatographic Conditions

The detection of biologically important compounds such as dopamine has been described on numerous occasions at carbon electrodes[1-8,13-17,43]. For many reasons

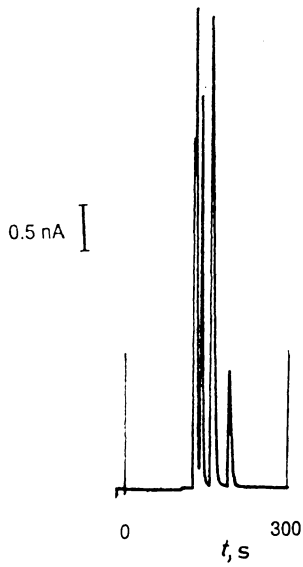

FIG. 5

Two-dimensional chromatogram (flow rate 1 ml min^{-1}) obtained at a 10 μm diameter platinum microelectrode with the thin layer electrochemical detector cell run in the amperometric mode (detection at +1·4 V vs Ag/AgCl). The compounds in elution order are adrenaline, 6-hydroxydopa, dopa, dopamine and tyrosine

platinum microelectrodes are less desirable than carbon microelectrodes for detection of such compounds. However, platinum electrodes can be used to illustrate that all the techniques previously used for data treatment of peak shaped curves (linear

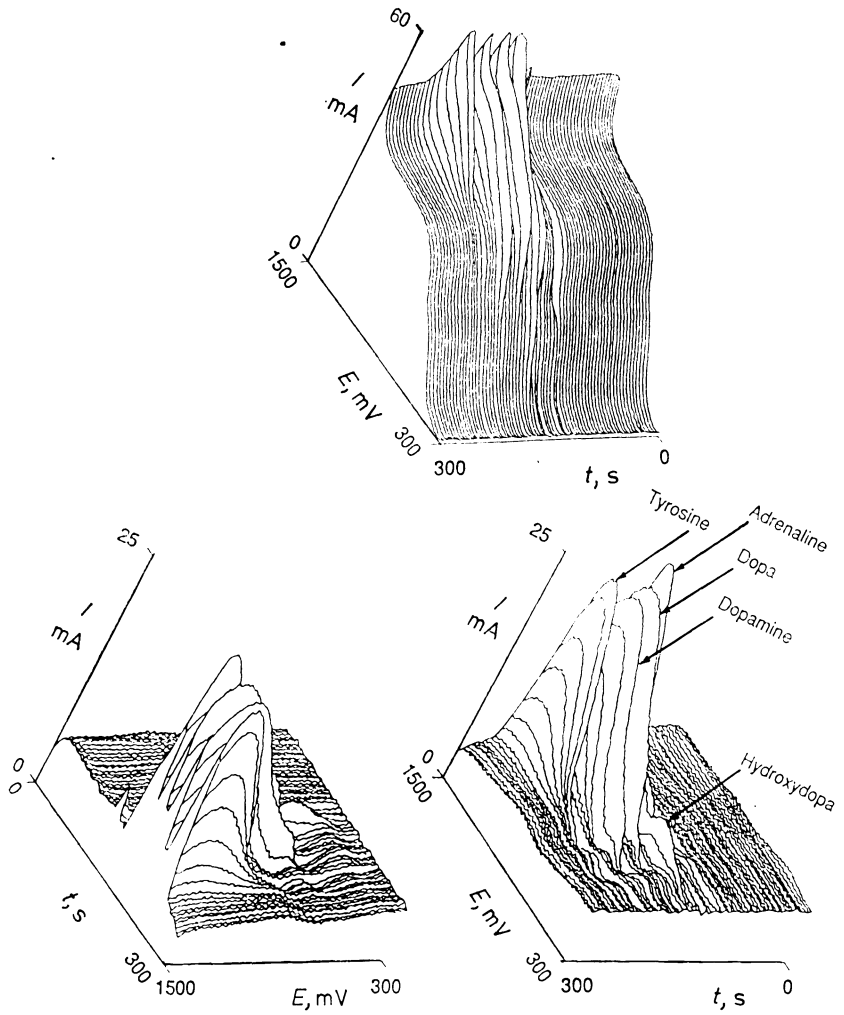

FIG. 6

Three-dimensional chromatograms obtained in a thin layer cell with a 10 μm platinum electrode. The elution order is adrenaline, 6-hydroxydopa, dopa, dopamine and tyrosine. A scan rate of 2 V s^{-1} and flow rate of 1·0 ml min^{-1} were used. The top chromatogram is before background subtraction. The bottom chromatograms are different viewpoints of the data after background subtraction

diffusion) are still applicable to fast scan steady state or near-steady state conditions. Figure 5 shows a conventional chromatogram of five biologically important compounds; adrenaline, 6-hydroxydopa, dopa, dopamine and tyrosine, as detected in the amperometric mode at a platinum microdisk electrode at a constant potential of +1·4 V vs Ag/AgCl. In the time domain, the chromatography is inadequate to baseline resolve the first peak, which is a mixture of adrenaline and 6-hydroxydopa. However, use of either a three-dimensional chromatogram (Fig. 6) or contour map (Fig. 7) allows adrenaline and 6-hydroxydopa to be easily resolved in the potential domain using the steady state rapid scan method developed in this work. The potentials at which each compound is oxidised is seen to match the data reported in the literature[6,27,44]. The mobile phase used in the chromatography is an aqueous phosphate buffer–methanol mixture. The large background signal at positive potentials again can be attributed to oxide film formation at a platinum electrode.

The plots in Figs 6 and 7 are different forms of presentation of the same data. The three-dimensional plot in Fig. 6 is the more traditional method of presenting this kind of data. It allows easy visual inspection of the results and is usually used for the preliminary examination of the area of the chromatogram of interest. However, the three-dimensional voltammetric detection plots are different to those presented by previous authors[7,8] in that the basic shape of the response is sigmoidal rather than peak shaped because of the minimal influence of linear diffusion even at a scan rate of 2 V s^{-1}. Also, because of the use of a micro-working electrode the voltammograms display little of the *iR* drop effect observed with conventionally sized electrodes[2].

The three-dimensional plot suffers from the fact that information may be hidden by larger neighbouring peaks, and peaks with similar half-wave potentials are diffi-

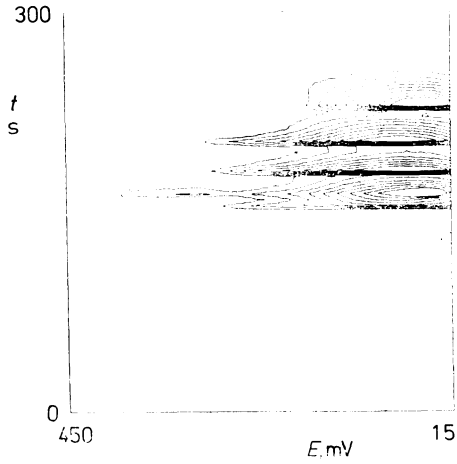

FIG. 7

A contour plot of the background subtracted chromatograms shown in Fig. 6. The minimum contour is 6·0 nA and maximum contour is 18·0 nA. The contour step is 1·5 nA

cult to distinguish. This problem may be minimised with the use of a contour map (Fig. 7), although the contour map is of a more discrete nature and therefore may lose information associated with small variations in current so that this representation is usually employed for qualitative rather than quantitative analysis.

The system reported under chromatographic conditions contains a mixture of biologically important compounds and was selected to demonstrate the operation of the steady state microelectrode detector under very difficult operating conditions. In a real application, a carbon rather than platinum microelectrode would be employed as noted above. At positive potentials with a platinum electrode there is a large background current present, which is not present at a carbon electrode. Additionally, the compound, 6-hydroxydopa is at a relatively low concentration, overlapping peaks are present (adrenaline and 6-hydroxydopa) and the mixture includes examples of compounds exhibiting slow electron transfer and adsorption, rather than electrochemical and chemical reversibility as is the case with oxidation of ferrocene. Each of these mechanistic complications are important in determining whether a microelectrode is a good detection system and further work is currently underway in these laboratories to elucidate the relationship between the mechanism and optimizing the detection techniques that should be employed for a given mechanism.

CONCLUSION

The electrochemical detector system designed in this work for use with microelectrodes under flowing solution conditions has been shown to be useful in both aqueous and non-aqueous solvents. However, non-aqueous work with the system described in this work is limited to solvents which have minimal effect on both the perspex block and the Torr seal used as part of the microelectrode fabrication. The thin-layer cell design which is available in many laboratories allows for the convenient adaptation of a system originally designed for amperometric work to rapid scan three dimensional and other forms of chromatographic detection. The cell design, coupled with the fact that the detector system can be run indefinitely as data is transferred to a disk during the experiment, allows the detector to be used with a minimum of change necessary to the chromatographic system developed for constant potential amperometric detection. The fact that the steady state or close to steady state response can be retained at fast scan rates enables excellent sensitivity to be retained with minimal iR distortion for reversible processes and other processes exhibiting appropriate oxidation or reduction mechanisms.

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