

# Precision Linear Sweep and Cyclic Voltammetry at Submillimolar Substrate Concentrations

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A procedure has been developed for precision linear sweep and cyclic voltammetry (CV) measurements at substrate concentrations in the range 0.01–1.00 mM and voltage sweep rates between 0.1 and 1000 V s<sup>-1</sup>. The measurements include (1) reduction of the periodic noise originating from the power line by application of a phase-sensitive triggering technique, (2) elimination of the non-Faradaic current and the current caused by the presence of impurities by background subtraction, and (3) additional noise reduction and, if required, differentiation of the resulting voltammograms by application of a fast Fourier transform (FFT) procedure. The FFT filtering technique was found to be superior to the Savitzky–Golay 'moving least-squares polynomial fit' both in terms of accuracy and noise reduction capability.

The determination of the CV peak potential difference for the reversible reduction of anthracene and the quasi-reversible reduction of the iron–sulfur complex [Fe<sub>4</sub>S<sub>4</sub>(SPh)<sub>4</sub>]<sup>2-</sup> at 0.1 mM substrate concentrations in dimethyl sulfoxide serves to illustrate an application of the method. From the data obtained for the complex, the value of the heterogeneous charge transfer rate constant, *k*<sub>s</sub>, was determined to be (5.0±0.2)×10<sup>-3</sup> cm s<sup>-1</sup>.

The level of precision of potential sweep voltammetric measurements has increased considerably during the latest 10 to 15 years due to improvements in the electrochemical instrumentation and data-handling procedures.<sup>1–5</sup> So-called high precision measurements with standard deviations in the range 0.1–0.2 mV are typically carried out at stationary planar electrodes with diameters between 0.5 and 2 mm and involve voltage sweep rates (*v*) in the range 0.1 to 1000 V s<sup>-1</sup> and substrate concentrations between 0.5 and 5 mM.<sup>1–4</sup> However, in a number of cases it is necessary to carry out voltammetric measurements at concentrations much lower than ca. 0.5 mM, for example when the substrate is only sparingly soluble or when accurate voltammetric measurements in the 0.5 to 5 mM range are hampered by adsorption phenomena as is frequently observed during studies of substrates with high molecular weights or substrates containing one or more highly polarizable atoms. Moreover, there is a general need for expansion of the substrate concentration range towards lower values during kinetic studies of otherwise well behaved substrates such that reaction order measurements<sup>1–4</sup> may be carried out also at the submillimolar concentration level. It is, however, not a trivial task to carry out voltammetric measurements at low substrate concentrations owing to the small values of both the Faradaic-to-non-Faradaic current

ratio and the signal-to-noise ratio, and in addition, voltammetry at submillimolar concentrations requires solvents and supporting electrolytes of an almost inaccessible purity.

For the reasons given above, precise voltammetric data for important classes of substrates such as sparingly soluble aromatic compounds or the redox proteins and their model compounds are only available in a few cases. Therefore, the aim of the present work was to design a procedure that allows voltammetric measurements to be carried out to high accuracy and with a precision of ±0.5 mV or better, at substrate concentrations down to 0.01 mM by application of modern electrochemical instrumentation.

## Results and discussion

Applications of linear sweep voltammetry (LSV) and cyclic voltammetry (CV) are usually based on measurements of peak or derivative peak currents, *I*<sub>p</sub> and (d*I*/d*t*)<sub>p</sub>, peak potentials, *E*<sub>p</sub>, and peak shapes, for example through the potential differences *E*<sub>p/2</sub>–*E*<sub>p</sub> or *E*<sub>p/4</sub>–*E*<sub>p</sub>, where *t* is the time and *E*<sub>p/2</sub> and *E*<sub>p/4</sub> are the values of the potential at *I* equal to *I*<sub>p</sub>/2 and *I*<sub>p</sub>/4, respectively.<sup>1–7</sup> The problems to be dealt with in performing these types of measurements at low substrate concentrations are clearly illustrated in Fig. 1, which shows cyclic voltammograms for the reduction of anthracene (A) in dimethyl sulfoxide (DMSO) at *C*<sub>A</sub><sup>∞</sup> = 0.1 mM [Fig. 1(a)] and *C*<sub>A</sub><sup>∞</sup> = 0.01 mM [Fig. 1(b)]. At

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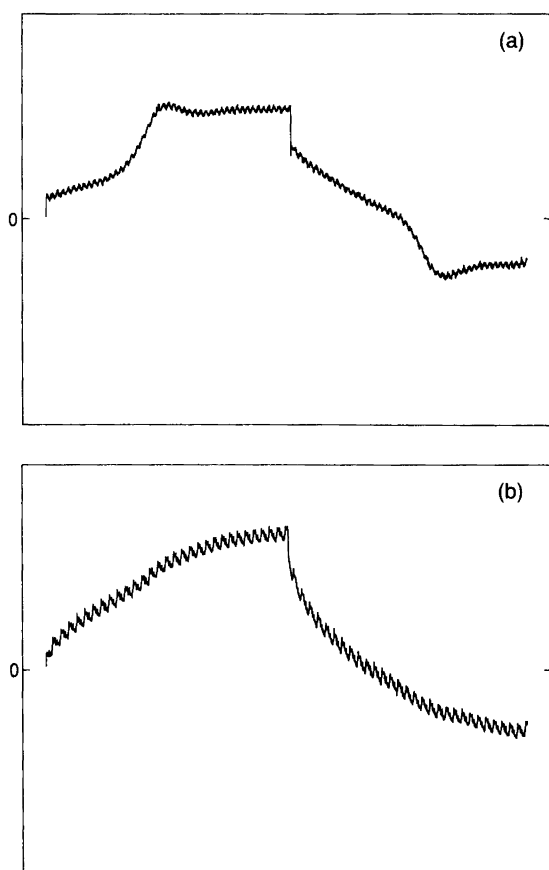


Fig. 1. Cyclic voltammograms recorded as current vs. time for the reduction of anthracene in dimethyl sulfoxide ( $0.1 \text{ M Bu}_4\text{NBF}_4$ ) at (a)  $C_A^0 = 0.1 \text{ mM}$  and  $v = 10 \text{ V s}^{-1}$  and (b)  $C_A^0 = 0.01 \text{ mM}$  and  $v = 1 \text{ V s}^{-1}$ . The voltage range was  $600 \text{ mV}$ .

the latter concentration the signal due to anthracene is barely visible and it is obviously meaningless to attempt to carry out conventional measurements under these conditions. The voltage range in these and all the following experiments was  $600 \text{ mV}$ .

Two additional features of the curves in Fig. 1 are of importance. First, it should be noted that the background current increases with decreasing potential in a non-linear fashion and evidently cannot be approximated by the equation for simple double-layer charging, eqn. (1), in which  $I_c$  is the charging current and  $C_d$  is the double-layer capacity assumed to be independent of the potential. This may in part be due to Faradaic contributions to the background current caused by reduction of impurities. Second, it was observed, not unexpectedly, that an appreciable part of the noise in the voltammogram was periodic with a period of  $20 \text{ ms}$  corresponding to that of the  $50 \text{ Hz}$  sine wave of the power line.

$$I_c = vC_d \quad (1)$$

Since the problems associated with low concentration measurements appear to be of very diverse nature and

since in particular the non-ideal contributions to the background current may be caused by the presence of small and variable amounts of impurities we decided to take an essentially empirical approach to minimize the unwanted contributions to the substrate current. This approach includes (1) reduction of the periodic noise by help of a phase-sensitive triggering technique, (2) elimination of the non-Faradaic current and the current caused by the presence of impurities by careful background subtraction, and (3) additional noise reduction and, if required, differentiation of the resulting voltammograms by application of a fast Fourier transform algorithm.

*Reduction of the periodic noise.* Averaging is a powerful way of diminishing the effect of the random noise associated with electrochemical measurements and is for that reason an indispensable part of all precision voltammetric techniques.<sup>2</sup> In our laboratory, measurements are initiated with preset time intervals by a homemade external trigger box, and the averaging of three to five measurements is generally sufficient to reduce the effect of the random noise to an acceptably low level. However, it has been observed repeatedly that when this particular trigger box is used the signal averaging leaves some of the periodic noise unchanged. This is easily explained when it is considered that the time unit of the trigger is exactly one period of the power line sine wave which means that much of the periodic noise picked up from external sources during one particular experiment will be recorded in-phase with the noise of the previous measurements. A slight modification of the trigger design such that every second measurement was triggered with a time delay of  $10 \text{ ms}$ , corresponding to half a period of the sine wave, caused this part of the periodic noise to cancel effectively provided the average included an even number of measurements (see Appendix 1 for a short description of the trigger design). Typical background curves resulting from the application of the modified trigger are shown in Fig. 2. Here and in the following, the average of four signals was used. Comparison of the noise levels of the curves in Fig. 1(b) and Fig. 2(a), which, except for the presence of substrate [Fig. 1(b)], were recorded under the same conditions, shows the effectiveness of the method. However, complete removal of the periodic noise could not be accomplished in this way due to the presence of overtones and other high frequency noise not in phase with the power line sine wave, but the amplitudes of these components were found, as the rule, to be notably smaller than that of the  $50 \text{ Hz}$  signal and the in-phase overtones.

Although no claim is made for the originality of this trigger technique we wish to emphasize its general utility not only in LSV and CV, but in most types of electroanalytical experiments. The method has recently been further developed.<sup>8</sup>

*Elimination of the background current.* The problem of separating the part of the current due to the oxidation or

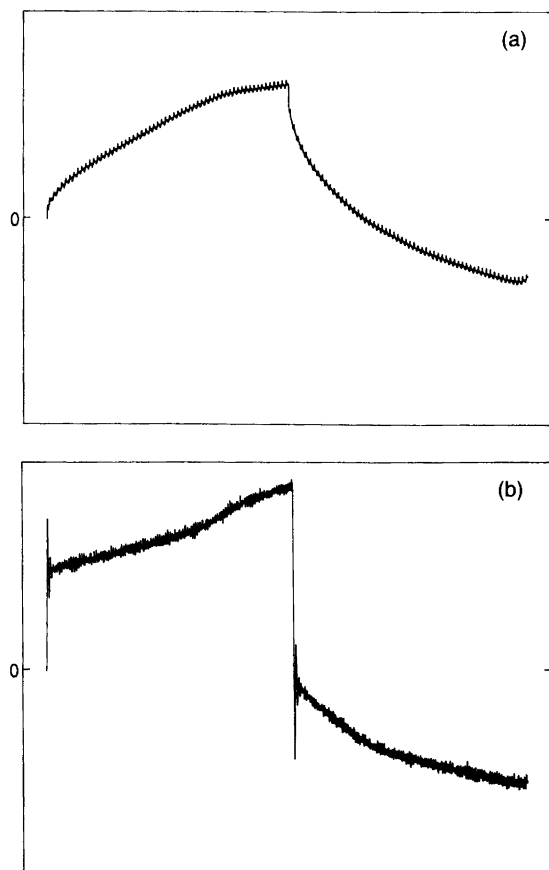


Fig. 2. Average of four background curves at (a)  $\nu = 1 \text{ V s}^{-1}$  and (b)  $\nu = 100 \text{ V s}^{-1}$  obtained by application of the trigger described in Appendix 1. The solution was dimethyl sulfoxide (0.1 M  $\text{Bu}_4\text{NBF}_4$ ) and the voltage range was 600 mV.

reduction of the substrate from the total signal is also encountered during CV at ultramicroelectrodes at sweep rates in the  $\text{kV s}^{-1}$  or  $\text{MV s}^{-1}$  range and has for that reason received considerable attention.<sup>9-11</sup> However, the substrate concentration during fast-sweep CV is usually between 1 and 10 mM and under those conditions the contributions from unknown impurities are negligible and experience has shown that the background current is adequately described by eqn. (1) and accordingly the problem of its elimination may be treated rigorously.<sup>10</sup> Unfortunately, this is not possible at the submillimolar concentration level and the only rational solution to the problem under those conditions appears to be application of an arithmetic background subtraction procedure similar to that described in other papers<sup>9,12,13</sup> to which the reader is referred for discussions of different aspects of this problem.

The procedure involves recording and digital storage of the current-voltage curve in the absence of substrate and this signal is then subtracted from the voltammogram recorded later under the same conditions in the presence of substrate. The measurement strategy relies on the assumption that the background current is not significantly affected by addition of substrate, and this is generally true at

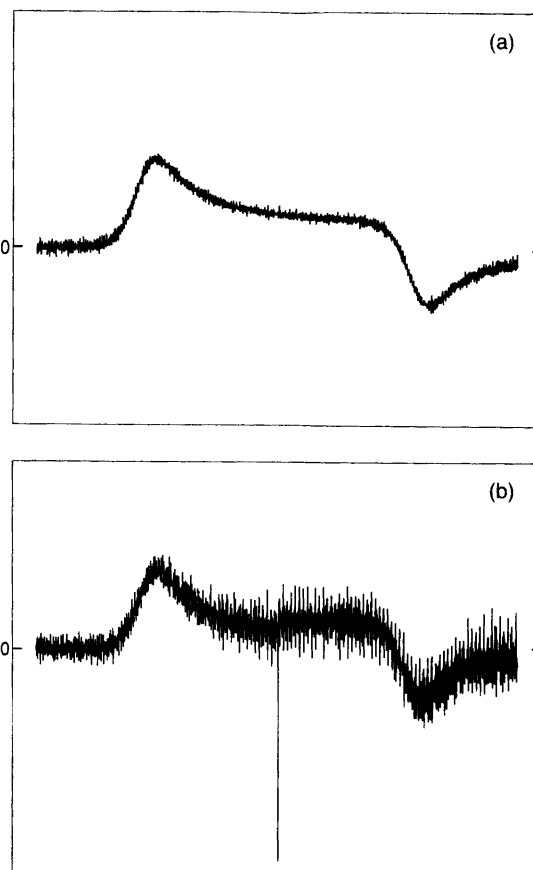


Fig. 3. Cyclic voltammograms of anthracene in dimethyl sulfoxide (0.1 M  $\text{Bu}_4\text{NBF}_4$ ) at a voltage range of 600 mV and (a)  $C_A^0 = 0.1 \text{ mM}$  and  $\nu = 100 \text{ V s}^{-1}$  and (b)  $C_A^0 = 0.01 \text{ mM}$  and  $\nu = 1 \text{ V s}^{-1}$ . The voltammograms are averages of four current-voltage curves from which are subtracted the average of four background curves, all obtained by application of the trigger described in Appendix 1. The current amplification of curve (b) is ten times that of curve (a).

low substrate concentrations and in the absence of specific adsorption. In addition, it is obviously necessary that the background current-voltage curves at a given sweep rate are highly reproducible. Our experience has shown that reproducible background curves can be obtained only if the solvent-supporting electrolyte solution is carefully deaerated by nitrogen purging for at least 20 min and the working electrode-solution interface has been brought to a steady state by repetitive voltage scans in the specific potential range of interest. This again calls for reference electrodes of extreme stability.

A result of the background subtraction procedure is shown in Fig. 3 for the reduction of A in DMSO at  $C_A^0 = 0.1 \text{ mM}$  and  $\nu = 100 \text{ V s}^{-1}$  [Fig. 3(a)] and  $C_A^0 = 0.01 \text{ mM}$  and  $\nu = 1 \text{ V s}^{-1}$  [Fig. 3(b)]. The difference between the voltammograms in Fig. 1(b) and Fig. 3(b) for  $C_A^0 = 0.01 \text{ mM}$  illustrates the effectiveness of the method. In particular it should be noted that the baselines of the voltammograms in Fig. 3 appear indeed to be very flat without significant curvature and that the current jump normally observed at the switch potential has been essen-

tially eliminated. We have found that the procedure works satisfactorily at substrate concentrations in the range 0.01–1.00 mM at sweep rates between 0.1 and 1000 V s<sup>-1</sup>.

A general problem in low concentration measurements is the poor current resolution caused by the fact that the Faradaic current due to reduction or oxidation of substrate is usually much smaller than the difference between the maximum and minimum values of the background current [see for example Fig. 1(b)]. This is particularly severe at fast sweep CV, where the current jump at the switch potential may take very large values compared with  $I_p$  owing to the fact that  $I_c$  is proportional to  $v$ , eqn. (1), whereas the Faradaic current is only proportional to  $v^{1/2}$ . This means that the Faradaic current will be only a small fraction of the current range necessary for keeping the entire voltammogram on scale at the recording instrument. In this study a 12 bit oscilloscope was used and we have found, as a rule of thumb, that a current resolution of 1% can be obtained if the maximum sweep rate,  $v_{\max}$ , for a particular solution is kept below  $10^5 (C_A^\circ/\text{mM})^2$  for well behaved Nernstian redox systems with diffusion coefficients of the order  $10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>. This means that the value of  $v_{\max}$  should preferably not exceed 1000 V s<sup>-1</sup> at  $C_A^\circ = 0.1$  mM and 10 V s<sup>-1</sup> at  $C_A^\circ = 0.01$  mM. For a redox system which gives rise to a smaller peak current, for example due to slow electron transfer and/or a small diffusion coefficient, the value of  $v_{\max}$  applied should be lowered accordingly.

This diminished current resolution during voltammetry at substrate concentrations in the submillimolar range is analogous to the inconvenience faced during fast sweep voltammetry, where the problem to some extent has been solved by the application of a capacitive offset, which compensates parts of the double-layer charging current before the signal is digitized.<sup>9</sup> We have not attempted to include this procedure in our measurements, but we wish to emphasize that some sort of offset technique is required if a recording instrument with a resolution of only 8 or 10 bits is used in this type of work.

Measurements of  $I_p$ ,  $(dI/dt)_p$  or  $E_p$  as a function of  $v$  are central in mechanism analysis by electrochemical methods.<sup>1-5</sup> In our experience these types of measurements at low substrate concentrations are best and most accurately carried out by recording and digital storage of an array of background curves, one for each sweep rate to be applied later in the presence of substrate. This may seem a somewhat tedious strategy, which obviously requires careful planning on the basis of results from preliminary experiments, but we are not aware of any other approach that competes in terms of accuracy for this particular purpose.

*Noise filtering and differentiation of voltammograms after background subtraction.* Reduction of noise by application of an analog low pass filter is a routine procedure during LSV and CV with substrate concentrations in the millimolar range. Our experience with the PAR model 189 selective amplifier used as a noise filter in the low pass mode has shown that a filter frequency (in Hz) of one hundred times

the sweep rate (in V s<sup>-1</sup>) may be applied without detectable distortion. However, the much smaller signal-to-noise ratio associated with low concentration measurements requires truncation of noise frequencies very close to those of the voltammetric curve. This excludes the application of analog low pass filters, which are characterized by having non-rectangular filter functions<sup>14,15</sup> and accordingly, efficient filtering of noise frequencies close to those defining the signal will inevitably cause distortion of the voltammogram. This calls for the application of a digital filtering procedure.

Fourier transform (FT) techniques have been widely applied, in particular in spectroscopy, for noise filtering, differentiation, convolution and other forms of data manipulation, and highly efficient hardware and software routines are now available for these purposes.<sup>16,17</sup> The use of the FT technique in electrochemistry has received much less attention<sup>11,18</sup> although Smith and co-workers as early as 1973 demonstrated the application of FT to a number of electrochemical techniques.<sup>19</sup> The great advantage of noise filtering by FT compared with the application of analog low pass filters is the possibility of using well defined filter functions.

Although the application of FT for filtering purposes is wide spread, a step-by-step procedure for application in LSV and CV has not been presented in the literature. For this reason a brief description of the FT technique is included in the following and some of the details associated with its application to the filtering of voltammograms during precision measurements are highlighted.

The fast Fourier transform (FFT) algorithm is a computationally fast version of eqn. (2), which defines the discrete Fourier transform,  $\mathbf{H}(n)$ ,<sup>20</sup> where  $i$  is the square root of  $-1$  and  $\mathbf{h}(k)$  is the digital representation of the voltammogram, described by  $N$  points sampled with the time interval,  $\Delta t$ , corresponding to a resolution of  $\Delta t/\text{point}$  in the time domain. The distance between the points in the frequency domain,  $\Delta f$ , i.e., the resolution in this domain, is related to  $\Delta t$  and  $N$  by eqn. (3).

$$\mathbf{H}(n) = \sum_{k=0}^{N-1} \mathbf{h}(k) \exp(-i2\pi nk/N); \quad n = 0, 1, \dots, N-1 \quad (2)$$

$$\Delta f = (N\Delta t)^{-1} \quad (3)$$

Simple FFT routines require  $N = 2^m$ ,  $m$  being an integer,<sup>20,21</sup> and in the following  $N = 2^{11} = 2048$  has been used to represent the essential parts of a cyclic voltammogram covering a sweep of 600 mV in each direction with a resolution of 0.5 mV/point.

In the application of FFT routines it is important that the data set begins and terminates with zero or near zero values, which a cyclic voltammogram, or a part of it, normally does not. Non-zero values of  $I$  at  $k = 0$  and  $k = N-1$  are recognized by the FFT routine as transients resulting in a broadband Fourier spectrum.<sup>19</sup> After truncation of the

spectrum by a rectangular low pass filter followed by inverse FT, the original transient may appear as ringing in the noise-filtered voltammogram, which for that reason may not be applicable for precision measurements. A simple modification of the original data prior to Fourier transformation analogous to the 'rotate-translate' procedure described by Smith and co-workers<sup>19</sup> was found to solve this problem. The modification involves subtraction of the straight line,  $y(k)$ , defined by eqn. (4) from the voltammogram, where  $h(0)$  is the first point and  $h(N-1)$  the last point of the part of the voltammogram to be transformed.

$$y(k) = \{[h(N-1) - h(0)]/N\}k + h(0) \quad (4)$$

The approach is illustrated in Fig. 4, which shows a cyclic voltammogram obtained by digital simulation, before [Fig. 4(a)] and after [Fig. 4(b)] subtraction of the 'zeroing line',  $y(k)$ . In practical work an average of 10 to 20 points around the first and the last point, respectively, was used to define the values of  $h(0)$  and  $h(N-1)$  in order to minimize the influence of noise in the determination of these two values.

From eqn. (2) it appears that the Fourier transform is a complex function. The real and imaginary parts of the

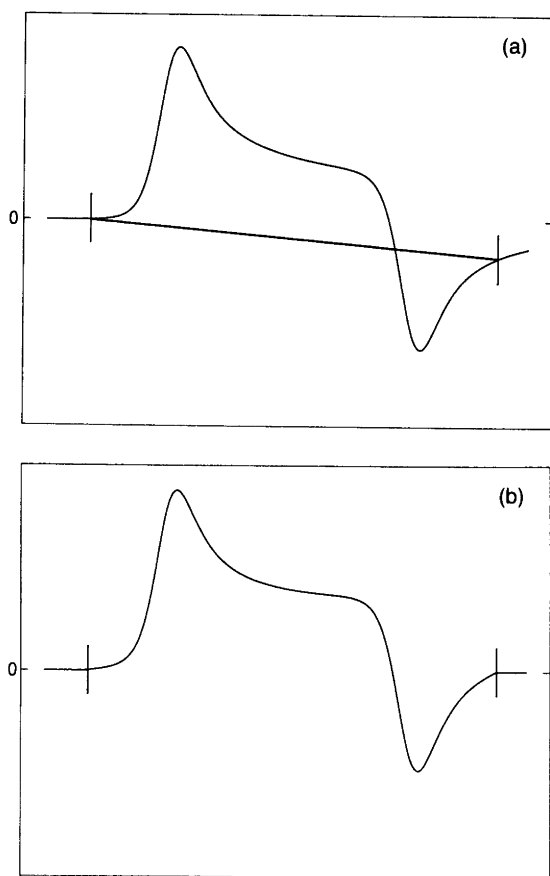


Fig. 4. Simulated voltammogram for a Nernstian one-electron reduction (a) before and (b) after subtraction of the 'zeroing line',  $y(k)$ , also shown in (a). The vertical marks indicate the range covered by  $N = 2048$  at 0.5 mV/point.

Fourier transform of the modified voltammogram are shown in Fig. 5 and it is seen that the voltammogram depicted in Fig. 4(b) is represented by only a few low frequencies of the full Fourier spectrum. As a result of an extensive series of measurements we have found that practically no information is lost if all frequencies except for the 20 lowest, positive and negative, are set to zero (see later). This frequency cut corresponds to the application of a low pass filter with the ideal rectangular filter function shown in Fig. 6(a).

The effect of this frequency cut on the shape of the voltammogram was tested by comparison of the original simulated data with the filtered data,  $h_f(k)$ , obtained by inverse Fourier transform of  $H_f(n)$ . The discrete inverse Fourier transform is defined by eqn. (5), but in practice the equivalent eqn. (6) is used,<sup>20</sup> which allows the inverse transformation to be carried out by the same computer routine as that used for the original transformation. Here  $h_f(k)$  is the digital representation of the filtered voltammogram and  $H_f^*(n)$  is the complex conjugate of  $H_f(n)$ .

$$h_f(k) = N^{-1} \sum_{n=0}^{N-1} H_f(n) \exp(i2\pi nk/N); \quad k = 0, 1, \dots, N-1 \quad (5)$$

$$h_f(k) = N^{-1} \left[ \sum_{n=0}^{N-1} H_f^*(n) \exp(-i2\pi nk/N) \right]^*; \quad k = 0, 1, \dots, N-1 \quad (6)$$

The voltammogram obtained after inverse FT of the frequency data filtered as described above and addition of the 'zeroing line' is shown in Fig. 7(a) and the arithmetic difference between this and the original voltammogram is shown in Fig. 7(b). It is seen that the difference between the two signals is indeed very close to zero. Furthermore, evaluation of the shapes of the two voltammograms by application of conventional measurements procedures<sup>4,6,7</sup> resulted in identical data within a measurement precision of  $\pm 0.1$  mV. Together these tests indicate that no measurable distortion has been introduced by the frequency cutting procedure.

One property of the Fourier transformation is that the transform of a real function has an even real part and an odd imaginary part<sup>20</sup> (see for example Fig. 5), and from eqn. (5) or (6) it follows that the imaginary part does not contribute to the inverse FT. Therefore, FFT algorithms designed specifically for real functions<sup>20,21</sup> may be used at this place in order to save computer time. However, the imaginary part cannot be neglected if the first derivative of the original signal is required. This follows from eqns. (7a) and (7b), which show the relationship between  $H(n)$  and  $H'(n)$  for the positive and the negative frequencies, respectively,<sup>17,22</sup> where  $H'(n)$  is the Fourier transform of the first derivative,  $h'(k)$ .

$$H'(n) = i2\pi n H(n); \quad n = 0, 1, \dots, N/2-1 \quad (7a)$$

$$H'(n) = i2\pi(N-n)H(n); \quad n = N/2, \dots, N-1 \quad (7b)$$

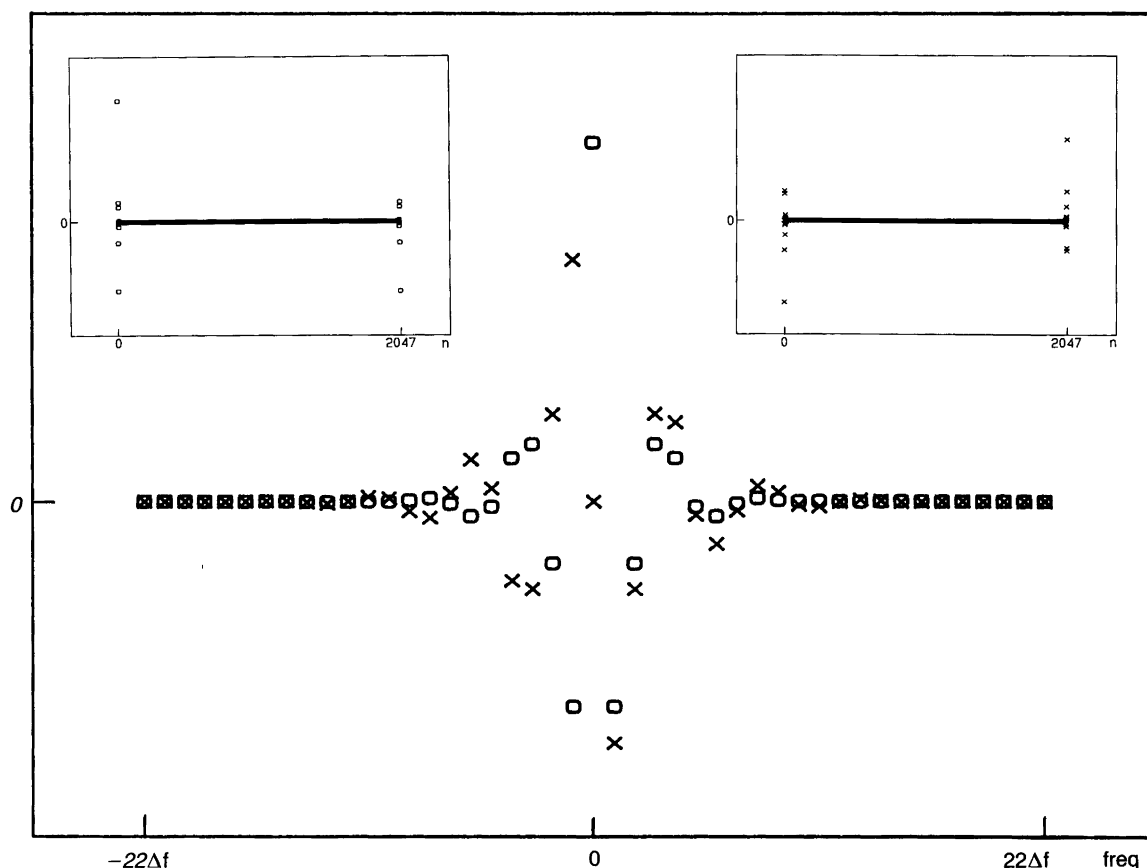


Fig. 5. The low-frequency end of the real (O) and imaginary (x) part of the Fourier transform of the voltammogram shown in Fig. 4(b). The inserts show the real part (left) and imaginary part (right) of the full Fourier spectrum,  $H(n)$ .

The effect of the filter function defined by eqns. (7a) and (7b) is an attenuation of the Fourier spectrum by a factor inversely proportional to the frequency as shown in Fig. 6(b). The fact that differentiation accentuates the weights of the high frequencies relative to the low frequencies emphasizes the importance of careful adjustment of the cut-off frequency prior to differentiation since it is primarily the highest remaining frequencies that contain noise contributions.

The result of the combined noise filtering and differentiation, using the same cut-off frequency as above, fol-

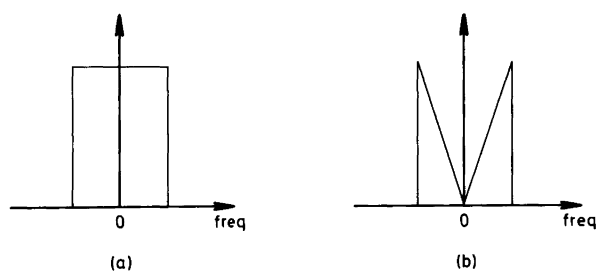


Fig. 6. Illustration of the filter functions to be applied to the Fourier transform for (a) noise reduction, and (b) noise reduction and differentiation.

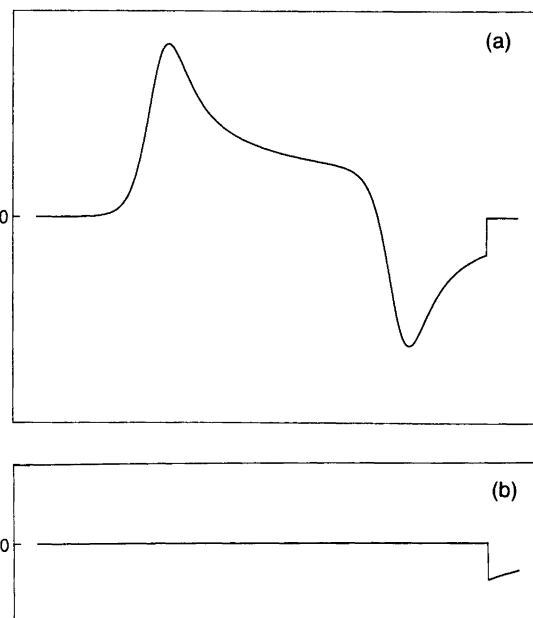


Fig. 7. (a) Voltammogram obtained after filtering of the real and imaginary parts shown in Fig. 5 as described in the text followed by inverse FFT and addition of the 'zeroing line'. (b) The arithmetic difference between the original voltammogram in Fig. 4(a) and the filtered voltammogram in Fig. 7(a) depicted on the same vertical scale as in Fig. 7(a).

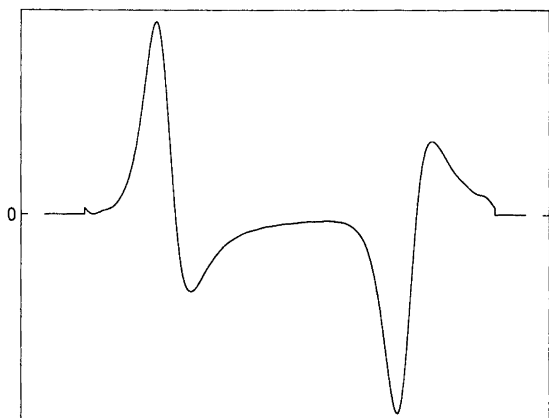


Fig. 8. The first derivative of the simulated voltammogram in Fig. 4(a) obtained by filtering and differentiation of the real and imaginary parts shown in Fig. 5 followed by inverse FFT and addition of the differentiated 'zeroing line'.

lowed by inverse FT and addition of the *differentiated* 'zeroing line', eqn. (8), is shown in Fig. 8.

$$y'(k) = [\mathbf{h}(N-1) - \mathbf{h}(0)]/N \quad (8)$$

The slight ringing observed at each end of the curve is a result of a 'too low' cut-off frequency and may be diminished by use of a higher value, but this would obviously result in less effective noise filtering and the actual choice of the cut-off frequency is therefore always a compromise. However, the zero-crossing potential and the heights and positions of the peaks of the first derivative, which are the parameters of major interest in most mechanistic and kinetic work, are the same as those measured directly from a derivative curve obtained by simple differentiation of the simulated voltammogram. In terms of practical work our experience is that the contributions from the noise remaining after filtering generally is more significant than the ringing caused by a 'too low' cut-off frequency and it was therefore decided to use the same frequency for both filtering and differentiation.

From eqn. (3) it follows that the cut-off frequency applied above for the simulated voltammograms corresponds to a frequency (in Hz) of 20 times the voltage sweep rate (in  $\text{V s}^{-1}$ ). From Fig. 5 one might get the impression that a cut-off frequency somewhat lower than 20 may be used and a factor of 12 has indeed been used by others.<sup>11</sup> Close inspection of Fig. 5 reveals, however, that the amplitudes of the signals in the frequency range  $12\Delta f - 20\Delta f$  are not all negligible and comparison of theoretical data before and after the FFT procedure shows that the error in peak potential measurements introduced by application of a factor of 12 amounts to approximately 2 mV for a Nernstian one-electron process, which is certainly respectable in many contexts. On the other hand, a cut-off frequency much less than  $20\nu$  is not adequate when the procedure includes the differentiation step, since differentiation accentuates the weight of the high frequencies relative to the

low as discussed earlier. If the heterogeneous electron transfer process is accompanied by a homogeneous chemical process prior to or following the electron transfer process, the resulting voltammogram will often have a shape that is significantly different from that of the voltammogram for a simple Nernstian process and accordingly the optimal cut-off frequency may differ from the value of  $20\nu$  recommended above. For precision work carried out in such cases it is recommended that the optimal cut-off frequency is determined from application of the filtering-differentiation procedure on a simulated voltammogram for the reaction scheme in question.

The voltammograms shown in Fig. 3 were used to examine the performance of the procedure during practical work. The results, which are shown in Fig. 9, demonstrate convincingly the capability of the FFT filtering procedure. An almost perfectly shaped voltammogram is obtained even at  $C_A^0 = 0.01 \text{ mM}$  and  $\nu = 1 \text{ V s}^{-1}$  where the signal-to-noise ratio of the unfiltered voltammogram is close to 4 [Fig. 9(b)]. Comparably good results were found for the combined filtering and differentiation procedure as shown in Fig. 10. Satisfactory agreement between the peak potentials of the filtered voltammograms and zero-crossings of the differentiated voltammograms was found at both sub-

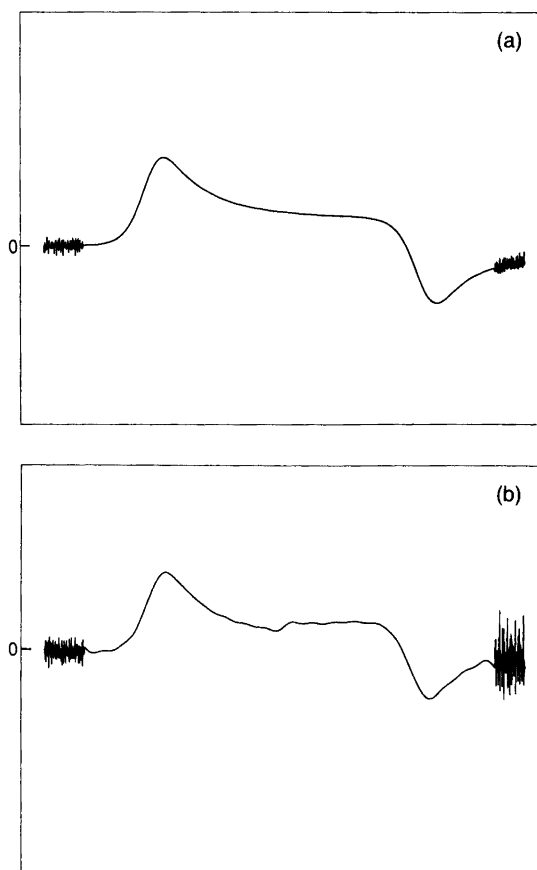


Fig. 9. Noise filtered voltammograms obtained by application of the FFT filtering procedure on (a) the voltammogram in Fig. 3(a),  $C_A^0 = 0.1 \text{ mM}$  and  $\nu = 100 \text{ V s}^{-1}$ , and (b) the voltammogram in Fig. 3(b),  $C_A^0 = 0.01 \text{ mM}$  and  $\nu = 1 \text{ V s}^{-1}$ .

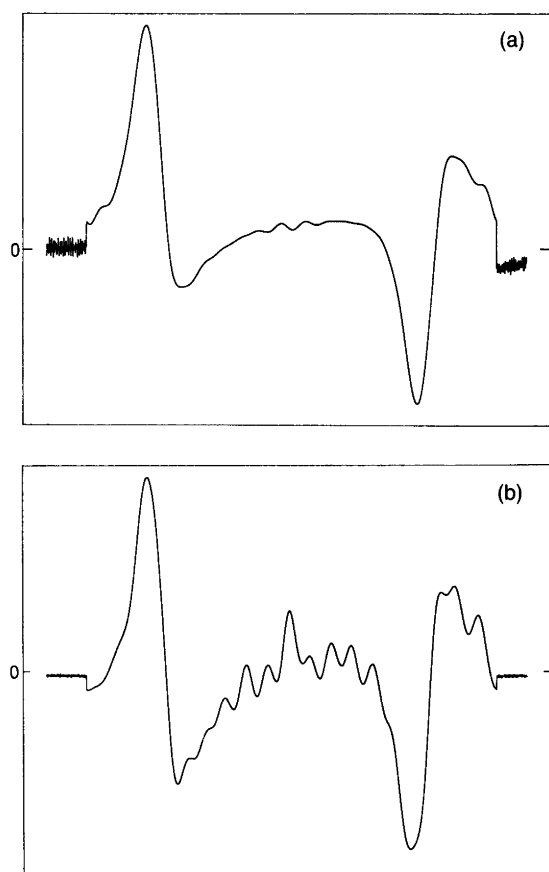


Fig. 10. Noise filtered and differentiated voltammograms obtained by application of the FFT filtering–differentiation procedure on (a) the voltammogram in Fig. 3(a),  $C_A^0 = 0.1$  mM and  $v = 100$  V s $^{-1}$ , and (b) the signal in Fig. 3(b),  $C_A^0 = 0.01$  mM and  $v = 1$  V s $^{-1}$ .

strate concentrations. Initially it was found that the maximum sweep rate,  $v_{max}$ , that can be used at low substrate concentrations was approximately  $10$  V s $^{-1}$  at  $C_A^0 = 0.01$  mM. At this sweep rate, where the signal-to-noise ratio is close to unity, the filtered voltammogram is still essentially free of noise (Fig. 11).

The conclusion drawn from these and other similar experiments is that the observed signal-to-noise ratio before filtering is of less importance for the quality of the final voltammogram than the precision by which the background subtraction is carried out. It should be noted that if the FFT procedure is used at substrate concentrations so high that baseline subtraction is deemed unnecessary, special care should be taken to avoid the effect of the transients observed at the switch potential. These transients will cause problems similar to those described resulting from non-zero initial and final values. However, this problem can easily be avoided if the voltammogram is initially divided into two sections, the forward and the backward scan, which are then treated separately, including subtraction of separate ‘zeroing lines’. The elimination of the transient in this way is compensated by a reduction of the resolution in the frequency domain by a factor of two; cf. eqn. (3). This,

however, causes no measurable effect on the resulting filtered voltammogram as long as the resolution of the recording instrument is kept at 1 mV/point or better.

*Comparison with Savitzky–Golay filtering.* At this point it seems appropriate to compare the FFT filtering with the mathematically more simple smoothing procedures based on moving least squares fits to polynomials. In a much cited paper, Savitzky and Golay<sup>23</sup> demonstrated the equivalence of this approach to a weighting of  $m$  equidistant points around a central point as expressed by eqn. (9). The weighting coefficients,  $c_i$ , are tabulated in Ref. 23. With another choice of coefficients the same procedure can be used for determination of the derivative of a noisy signal.<sup>23</sup> The close resemblance of this procedure to a moving average makes it intuitively more straightforward than the FFT method.

$$h_f(k) = \left[ \sum_{i=k-m/2}^{k+m/2} h(i) c_i \right] / \left[ \sum_{i=k-m/2}^{k+m/2} c_i \right] \quad (9)$$

It is obvious from eqn. (9) that the smoothing procedure becomes more time consuming the larger the number of points in the moving least-squares fit, but also that the smoothing effect is increased by an increasing number of points. The upper limit of the number of points that can be included in the smoothing is, in addition to the computer time involved, determined by the shape of the signal compared with the order of the polynomial. If so many points are included in the least-squares fit that the signal cannot be approximated by the selected polynomial within the range defined by the first and the last point, the resulting signal will be distorted. Application of a 25 point quadratic/cubic moving least-squares fit to the background subtracted voltammogram obtained at  $C_A^0 = 0.1$  mM and  $v = 10$  V s $^{-1}$  [Fig. 12(a)], resulted in the smoothed voltammogram shown in Fig. 12(b). Comparison of this voltammogram

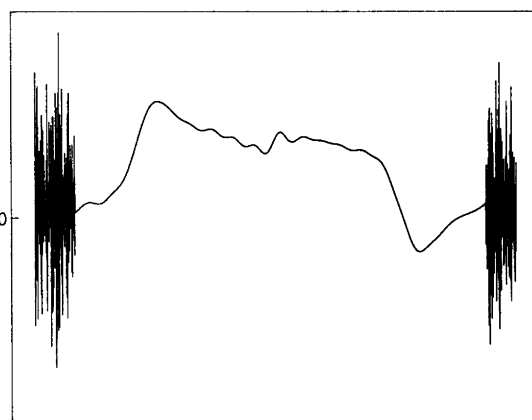
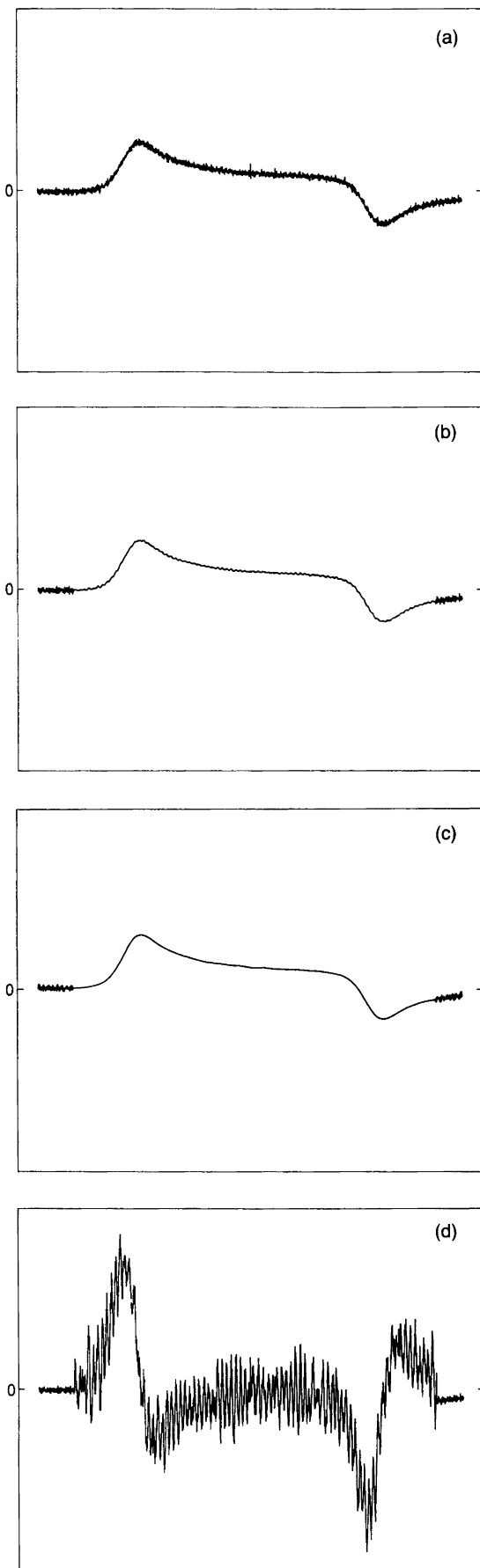


Fig. 11. Noise-filtered voltammogram obtained by application of the FFT filtering procedure at  $C_A^0 = 0.01$  mM and  $v = 10$  V s $^{-1}$  [same solution and voltage range as in Fig. 3(b)].





with that in Fig. 12(c) originating from FFT filtering illustrates the improvement offered by the latter procedure. It is seen from Fig. 12(b) that parts of the noise are reproduced even when as many as 25 points are used at a resolution of 0.5 mV/point. Preliminary tests with simulated data at a resolution of 0.5 mV/point demonstrated that an extension of the filter to encompass 51 points<sup>24</sup> caused minor but significant distortions of the voltammogram, and even in this case the result is inferior to that obtained by the FFT procedure in terms of the noise remaining.

Application of a 25 point moving least-squares procedure with coefficients designed to give the first derivative of the signal was likewise tested on the voltammogram in Fig. 12(a) and the resulting curve is shown in Fig. 12(d). Sequential application of smoothing and differentiating least-squares digital filters improves the result, but not to an extent satisfactory for precision measurements and in addition, this approach is far more time consuming than the FFT procedure.

A final experimental test of the procedure described above included measurements of the peak separation,  $\Delta E_p = E_p^{\text{ox}} - E_p^{\text{red}}$ , for the voltammetric reduction of anthracene. This substrate exhibits almost ideal behaviour during CV and has for that reason been used extensively as a test substrate during the developments of new electrochemical techniques.<sup>1-3</sup> At a substrate concentration of 1 mM, where the Faradaic-to-non-Faradaic current ratio and the signal-to-noise ratio are large, measurements of  $\Delta E_p$  could be carried out by application of both a conventional method<sup>7</sup> and the background subtraction-FFT procedure. The results, which are summarized in Table 1, demonstrate that essentially identical data sets are obtained for the same solution by the two methods at this concentration level. At the tenfold lower concentration, 0.1 mM, it was not possible to carry out meaningful conventional  $\Delta E_p$  measurements, but application of the baseline subtraction-FFT procedure resulted in data that, except for the value obtained at  $v = 100 \text{ V s}^{-1}$ , were practically the same as those obtained at  $C_A^0 = 1.0 \text{ mM}$ . These three sets of data substantiate the conclusion arrived at in the previous section that the baseline subtraction-FFT procedure does not introduce systematic errors in the measured quantities, here  $\Delta E_p$ , and furthermore show that precision voltammetric measurements may indeed be carried out at substrate concentrations much lower than those hitherto applied during CV.

Fig. 12. Voltammogram for reduction of anthracene at  $C_A^0 = 0.1 \text{ mM}$  and  $v = 10 \text{ V s}^{-1}$  (a) after baseline subtraction only; (b) after digital smoothing by application of a 25 point moving least-squares quadratic/cubic fit to the signal in (a); (c) after application of the FFT filtering procedure to the signal in (a); (d) after differentiation by application of a 25 point moving least-squares fit to the signal in (a) [same solution as the one used for Fig. 3(a)].

An example of a practical application of the procedure. Voltammetric measurements on compounds of high molecular weight or compounds containing one or more highly polarizable atoms, such as sulfur, selenium and phosphorus, are often hampered by adsorption problems as mentioned in the introduction. A typical example is the voltammetric reduction of the iron–sulfur complex,  $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$  (ISC), in DMSO at a platinum working electrode. The values of  $\Delta E_p$  obtained by the background subtraction–FFT procedure for a 1.0 mM solution of this compound are summarized in Table 2 for two subsequent series of measurements. Inspection of the data shows that the reproducibility is very poor, the values of  $\Delta E_p$  in the second series being larger than those of the first series by 16 to 22 mV. The origin of this behavior is not known for certain, but is likely to be related to an adsorption phenomenon. The reproducibility of the data was improved considerably when the substrate concentration was decreased by a factor of 10 to 0.1 mM as shown in columns 4 and 5 of Table 2. The maximum difference between the two series was reduced to less than 2 mV except at  $v = 2 \text{ V s}^{-1}$  where the difference amounts to 6.4 mV. What is even more important is that the differences take both positive and negative values indicating that these data are not affected to any significant extent by the phenomenon behind the poor reproducibility observed for the 1.0 mM solution. We find that these data illustrate the advantage of performing measurements on substrates of this kind at the lowest possible concentrations.

The access to peak separation data recorded at a series of different voltage sweep rates allows for the evaluation of the rate constant for heterogeneous charge transfer,  $k_s$ .

Table 1. Values of the peak separation,  $\Delta E_p$ , for the voltammetric reduction of anthracene, A, in dimethyl sulfoxide obtained by conventional cyclic voltammetry and by the baseline subtraction–FFT procedure.<sup>a</sup>

$v/\text{V s}^{-1}$	$(E_p^{\text{ox}} - E_p^{\text{red}})/\text{mV}$		
	$C_A^0/\text{mM} = 1.0$		$C_A^0/\text{mM} = 0.1^b$
	conv. <sup>c</sup>	FFT <sup>d</sup>	FFT <sup>e</sup>
1	59.8	59.3	59.2
2	60.8	59.6	59.4
5	61.4	60.0	59.6
10	61.6	60.9	60.0
20	62.5	60.3	61.3
50	63.2	62.7	63.6
100	63.1	63.1	65.5

<sup>a</sup>Measurements carried out at an Hg/Pt working electrode ( $d = 0.6 \text{ mm}$ ). The supporting electrolyte was  $\text{Bu}_4\text{NBF}_4$  (0.1 M).

<sup>b</sup>Concentration too low for conventional precision CV measurements. <sup>c</sup>Measurements made on the average of four voltammograms using conventional procedures. <sup>d</sup>Measurements carried out on the same solution as used for the conventional measurements, but this time by the baseline subtraction–FFT procedure. <sup>e</sup>Measurements carried out using the baseline subtraction–FFT procedure.

The value of  $k_s$  was determined to be  $(5.0 \pm 0.2) \times 10^{-3} \text{ cm s}^{-1}$  by fitting the experimental data for  $C_{\text{ISC}}^0 = 0.1 \text{ mM}$  to the working curve<sup>25,26</sup> obtained by digital simulation for  $E^\circ - E_{\text{switch}} = 0.3 \text{ V}$  assuming  $\alpha = 0.5$  and  $D_{\text{ox}} = D_{\text{red}}$ . The value of  $E^\circ$  was taken as the midpoint between the cathodic and the anodic peak, and the diffusion coefficient,  $D_{\text{ISC}}$ , was determined from the peak height relative to that of anthracene at  $v = 0.1 \text{ V s}^{-1}$  to be  $3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  using the value  $D_A = 8.9 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ .<sup>27</sup>

## Experimental

**Chemicals.** Anthracene (Rhône-Poulenc, Prolabo, *pur*) was used as received. The iron–sulfur complex,  $(\text{Bu}_4\text{N})_2\text{Fe}_4\text{S}_4(\text{SPh})_4$ , was synthesized according to a literature procedure and kindly donated by Mogens L. Andersen. The supporting electrolyte,  $\text{Bu}_4\text{NBF}_4$ , was prepared as previously described.<sup>7</sup> Solutions of  $\text{Bu}_4\text{NBF}_4$  in dimethyl sulfoxide (Fluka, *purum*) were passed through a column filled with neutral alumina (Woelm, W 200) immediately before the voltammetric measurements were made.

**Cells, electrodes and instrumentation.** The voltammetric cell was a cylindrical tube (50 ml) fitted with a side-arm through which the substrate was added and a B29 joint to accommodate a plastic electrode holder equipped with a nitrogen inlet. The platinum working electrode was made from 0.6 mm wire sealed into soft glass and the mercury working electrode was prepared by electrolytic deposition of mercury at the surface of a platinum electrode. The potentiostat was a PAR model 173/276 driven by an HP 3314A function generator. The function generator was activated by the trigger system described in Appendix 1. The experimental data were recorded on a Nicolet oscilloscope, model 2090-3C/206-2. The function generator and

Table 2. Values of the peak separation,  $\Delta E_p$ , for the voltammetric reduction of  $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$  (ISC) in dimethyl sulfoxide.<sup>a</sup>

$v/\text{V s}^{-1}$	$(E_p^{\text{ox}} - E_p^{\text{red}})/\text{mV}$			
	$C_{\text{ISC}}^0 = 1.0 \text{ mM}$		$C_{\text{ISC}}^0 = 0.1 \text{ mM}$	
	1st series	2nd series	1st series	2nd series
0.1	103	119	86.2	85.8
0.2	118	135	97.4	96.9
0.5	142	158	113.6	113.3
1.0	165	181	134.7	136.6
2.0	197	219	166.4	172.8

<sup>a</sup>Measurements carried out at a Pt working electrode ( $d = 0.6 \text{ mm}$ ) by application of the baseline subtraction and FFT procedure. The peak potentials were measured as the zero-crossings of the first derivatives as described in the text. Two consecutive series of measurements with increasing sweep rates were carried out at each concentration without disconnecting the electrodes from the potentiostat between the two series. The supporting electrolyte was  $\text{Bu}_4\text{NBF}_4$  (0.1 M).

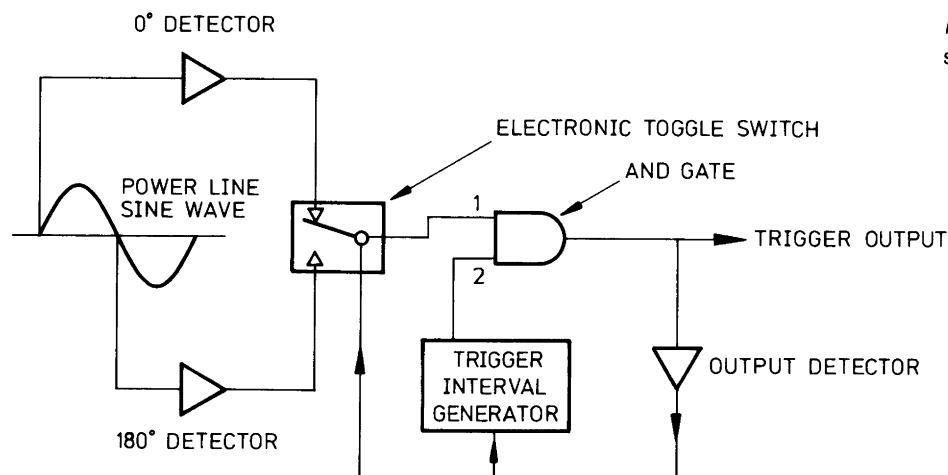


Fig. 13. Block diagram of the trigger system used in this study.

the oscilloscope were interfaced to an HP 9826A desk computer equipped with an HP 98635A floating point accelerator, an HP 9154A hard disc, an HP 2671G printer and an HP 7475A plotter.

**Software.** Programs for instrument control and all data-handling procedures, except for the FFT routine, were written in HP Basic 3.0. The FFT routine was written in HP Pascal 3.1, compiled and linked to the Basic program. For the sake of programming simplicity it was decided to use the standard FFT routine, which gives both the real and the imaginary part, in all cases, even though the imaginary part is not needed for noise filtering alone as discussed in the text.

**Measurement procedure.** The details of the measurement procedure are described in the text. The averaged baselines for each sweep rate were stored on the hard disc together with information about the oscilloscope settings and the measured resolution (mV/point).

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## Appendix 1

A block diagram of the trigger system used in this study is depicted in Fig. 13. Initially the number of seconds between each measurement is set on the trigger interval generator. When the electronic toggle switch is in the position shown in Fig. 13, the AND gate will produce a trigger pulse at the preset time synchronized with the zero-crossing of the rising part of the net sine wave detected by the 0° detector. This event is detected by the output detector, which causes the toggle switch to connect pin 1 of the AND gate with the

180° detector, and consequently, the next trigger pulse will be fired at the zero-crossing of the declining part of the net sine wave, i.e. with a time delay of 10 ms relative to the first pulse. This will cause the toggle switch to return to its initial 0° position and the entire procedure is repeated.

A detailed electronic diagram is available upon request from Mr. Svend Aage Laursen.

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