

Hilbert transform of voltammetric data

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Abstract

The use of the fast Fourier transform (FFT) assumes stationarity and, in many applications, linearity; assumptions that are often invalid in the analysis of voltammetric data. Empirical mode decomposition followed by the Hilbert transform offers an alternative mode of analysis that can overcome these difficulties. The validity of the Hilbert transform for the analysis of non-linear signals merits application to electrochemistry which, to our knowledge, has not been carried out before. Preliminary results, for three well-characterised redox processes: (i) a thermodynamically reversible electron transfer; (ii) formation of a passivating layer; (iii) growth of an oxide layer on an electrode surface, suggest that it can provide useful and novel insights into electrochemical processes. A less well-characterised process, the adsorption of 5-hydroxytryptamine (5-HT) oxidation products on the surface of a glassy carbon electrode, is also investigated using the Hilbert transform.

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1. Introduction

Sine wave voltammetry was investigated by Matheson and Nichols [1] and Matsuda [2] although triangular wave cyclic voltammetry has dominated the field [3]. The use of sinusoidal cyclic voltammetry has resulted in a more effective technique in the study of the mechanisms of electrode processes. Some of the advantages of ac over dc voltammetry have been given by Bard and Faulkner [4].

The fast Fourier transform (FFT) is an important tool for measuring the frequency content of a periodic signal. Cord and Smith [5] were the first to consider the advantages of analysing the second harmonic in ac polarography. Sine wave voltammetry was re-investigated by Long and Weber [6] and more recently by Kuhr et al. [7–9] who used the FFT to look at the second harmonic where the faradaic to non-faradaic ratios are more

favourable. Most impressively Kuhr et al. [8] used phase information to significantly improve the selectivity for (i) the overlapping redox couples ferrocene carboxylic acid (FCA) and ferrocene acetic acid (FAA) and (ii) the biomedically important but difficult problem of measuring oxidisable neurotransmitters against a high background of ascorbate. The theoretical basis for these excellent and potentially important results is not clear. The Hilbert transform that results in temporal information and is applicable to non-stationary and non-linear data may be significantly advantageous over the more conventional transforms.

Electrochemical processes are intrinsically non-linear and non-stationary and so the FFT is not applicable to the analysis of these types of data. It has been widely believed that the application of small sinusoidal perturbations give rise to linear data making it applicable for analysis by FFT [10–12] and the Kramers–Kronig transform [13] both of which result in a loss of phase data. In many cases FFT has been applied to the data ignoring the fact that the signal is non-linear where the harmonics may be lost in the noise. This is supported by

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Engblom et al. [14] who found that the application of small or large perturbations resulted in the same results which suggest that significant non-linearities remain in small amplitude perturbations. There is, therefore, a considerable advantage in applying large sinusoidal perturbations since the signal to noise ratio is significantly improved. This has been underlined most recently in a paper by Guo et al. [15] who looked at the ac voltammetry of surface bound azurin at a paraffin-impregnated graphite electrode and found that the higher harmonic Faradaic currents were significantly amplified when large sinusoidal perturbations were employed.

The major problem with the FFT is the stricture that the ac signal be linear, periodic or stationary. The fact that the linearity stricture practically invalidates the application of the FFT to electrochemical data has led us to empirical mode decomposition (EMD) and the application of the Hilbert transform, which is valid for non-linear data [16]. The EMD method has two main components; the calculation of the mode by subtraction of the instantaneous mean of the signal determined from the signal envelope and calculation of the instantaneous frequency of the resultant zero mean mode using the Hilbert transform. The main function of the EMD is to decompose the data into components, known as intrinsic mode functions (IMF), from which the instantaneous frequency can be defined. As a result there can be more than one instantaneous frequency at a time and each event can be localised on the time as well as the frequency axis.

The Hilbert transform creates the in-phase and quadrature components from the analytic waveform which in turn generates the phasor to give phase angle (θ) and amplitude information. Hence, the Hilbert transform results in instantaneous frequency ($d\theta/dt$) and amplitude as a function of time. Fig. 1 illustrates the advantage of the Hilbert transform for the analysis of non-stationary, non-linear signals, compared to the Fourier transform. Fig. 1(a) shows an exponentially increasing, linear chirp with the corresponding Hilbert amplitude plot (Fig. 1(b)) where the amplitude exponentially increases and the instantaneous frequency plot (Fig. 1(c)) which linearly decreases over time. However, the broad peak of the Fourier transform power spectrum (Fig. 1(d)) translates little information about the exponentially increasing, linear chirp (Fig. 1(a)) from which it is derived. The small deviation in amplitude and frequency at the beginning and end of the plots, in Fig. 1(b) and (c), are due to end effects.

Using three well-characterised model systems and one important neurotransmitter application we show how the Hilbert transform can provide useful and novel insights into electrochemical processes: (i) a fast electron transfer couple, hexaammineruthenium(III)chloride; (ii) the growth of an oxide layer on an iridium electrode [17]; (iii) the formation of a passivating layer using *p*-phenylenediamine [18,19].

We also looked at the neurotransmitter, 5-hydroxytryptamine (5-HT), where the response from the change in concentration was recorded and analysed using the Hilbert transform. Also known as serotonin, 5-HT is an oxidisable molecule found in the mammalian brain and has been associated with a number of mental disorders such as depression. Carbon fibre electrodes have been commonly used in the electrochemical detection of 5-HT and it has been found that at conventional scan rates the formation of an insoluble film of oxidation products of 5-HT and other hydroxindoles [20,21] results in a reduction in the sensitivity of the carbon electrode. The concentration range over which it occurs is somewhat uncertain and it is desirable to know whether the electrode functions correctly when implanted in vivo.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from BDH except for Tris-HCl and hexaammineruthenium(III)chloride which were purchased from Aldrich, *p*-phenylenediamine from Sigma and 5-HT from ICN Biomedicals Inc. All chemicals were used as received.

Three different concentrations (1, 4 and 8 mM) of hexaammineruthenium(III)chloride were made up in a 1 M KCl solution (−0.3 to 0 V vs. Ag/AgCl) and 10 mM *p*-phenylenediamine was made up in 0.1 M Na₂HPO₄ and 0.15 M NaCl and adjusted to pH 7.4 with 2 M HCl (0.4–0.9 V vs. Ag/AgCl). In both of the sinusoidal wave voltammetry (SWV) experiments above a 2 mm platinum disc electrode was used. The iridium electrode (−0.25 to 1.25 V vs. Ag/AgCl) was analysed in 0.5 M H₂SO₄ and 5-hydroxytryptamine was made up in a 0.15 mM Tris-HCl buffer adjusted to pH 7.9 with a 1 M NaOH solution (0–0.6 V vs. Ag/AgCl). SWV was carried out using a 3 mm glassy carbon electrode.

The 2 mm platinum and 3 mm glassy carbon electrodes used in the frequency experiments were purchased from CH Instruments (Austin, TX, USA). For all experiments sinusoidal perturbations were applied at a frequency of 1 Hz over a time period of 20 s and sampled at 100 Hz.

2.2. Data analysis

The Hilbert transform of a real signal, $X(t)$, is the signal, $Y(t)$, which makes the complex signal $Z(t) = X(t) + jY(t)$ analytic. It is calculated using the Fourier transform method [22] implemented as an algorithm in Matlab (The Mathworks, MA, USA). The complex signal $Z(t)$ is represented in polar form $Z(t) = A(t)e^{j\theta(t)}$ where $A(t)$ is the magnitude and $\theta(t)$ the phase of Z . The instantaneous frequency is defined as $\omega(t) = d\theta/dt$.

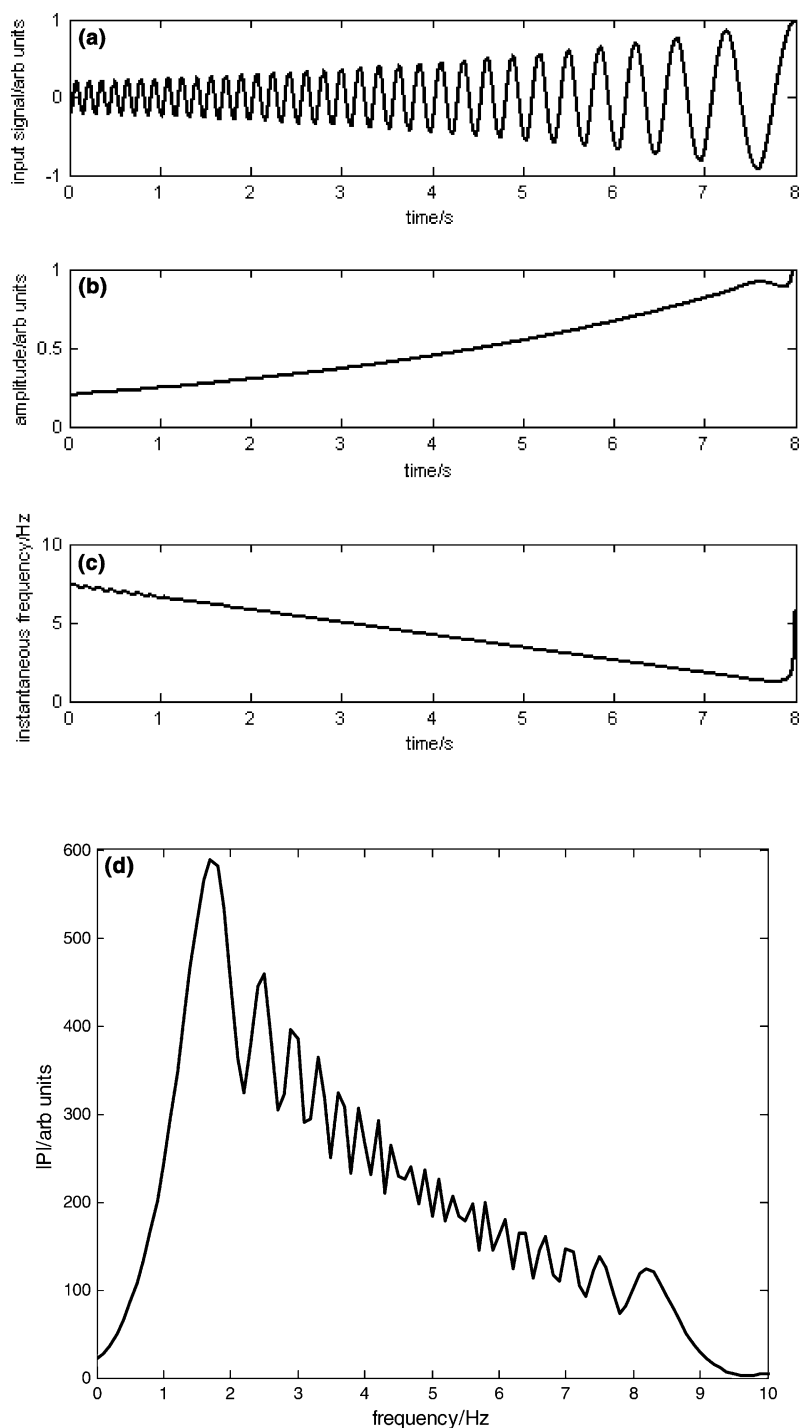


Fig. 1. (a) An exponentially increasing, linear chirp, 8–1 Hz, and the resulting (b) Hilbert amplitude and (c) Hilbert instantaneous frequency plot. (b) The amplitude exponentially increasing over time and (c) the instantaneous frequency linearly decreasing over time. (d) The Fourier transform for the chirp in (a).

Since the Hilbert transform is defined through differential relations, the Cauchy Riemann condition, it is unique only up to a constant, i.e. $H\{X\} = H\{X + C\}$. This is why it is important in the empirical mode decomposition to reduce the signal to modes that have a zero mean locally. It is essential that the phase, θ , be monotonically

increasing for the instantaneous frequency to be meaningful, which can only be realised for signals of zero mean.

A significant advantage of this mode of analysis is that it is carried out in the time domain. Both $A(t)$ and $\omega(t)$ are calculated as functions of time and can therefore be related to all temporal events during the measurement. In

particular, in voltammetry the instantaneous values of A and ω characterising the current $i(t)$ can be related to the instantaneous voltage, $V(t)$, and other characteristics such as whether the voltage is rising or falling.

2.3. Preliminary studies of three well-characterised processes

1. In the hexaammineruthenium(III)chloride experiments it was found that the Hilbert transform ampli-

tude, of the output current signal, changed linearly with concentration over the range 1–8 mM. However, the three corresponding Hilbert transform frequency plots overlay each other and are indistinguishable (data not shown). This shows that the Hilbert transform can reliably separate out factors affecting amplitude (concentration) from electrode rate parameters.

2. Anodically generated iridium oxide has been used in pH sensing [23–25]. Metal, metal oxide electrodes are robust alternatives to glass pH sensors [26] and

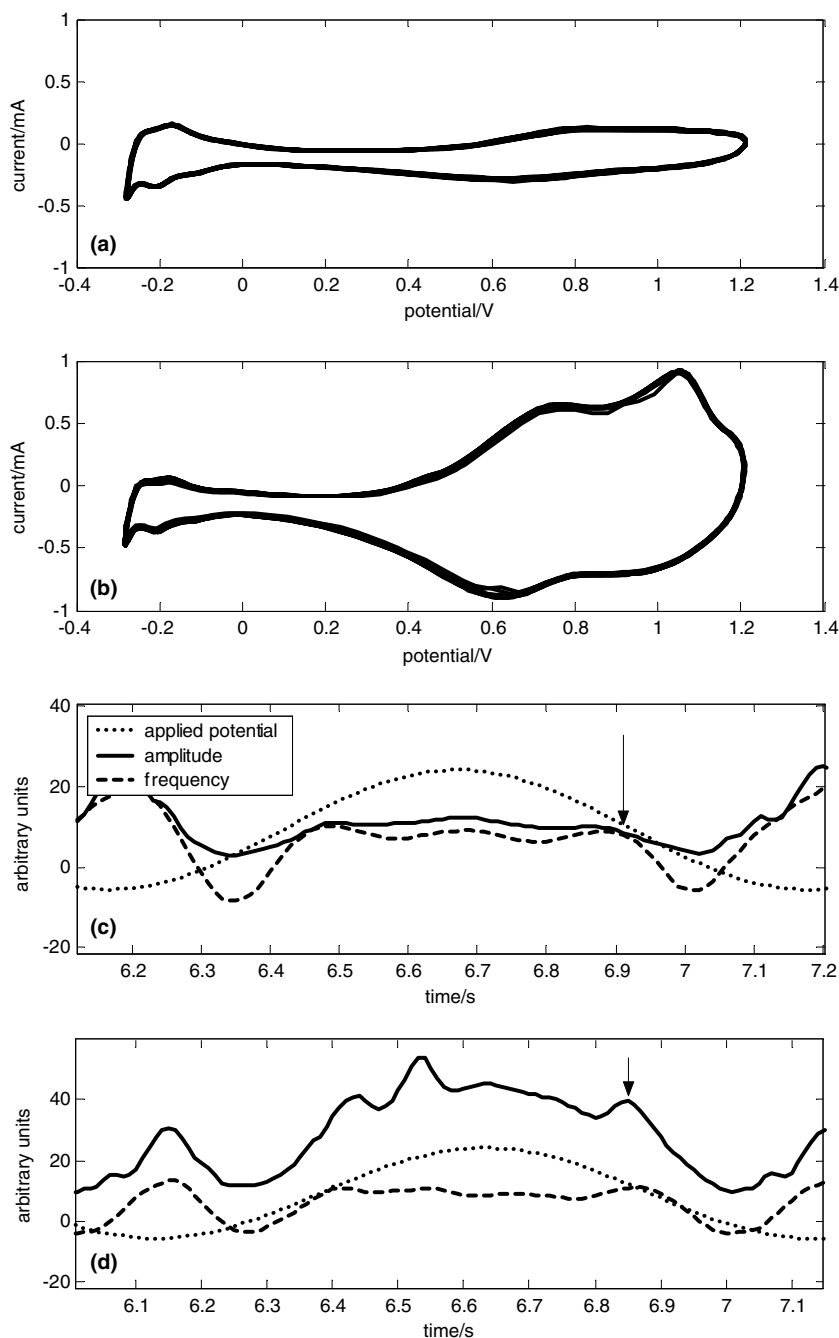


Fig. 2. SWV in (a) and (b) showing the hydrous oxide growth before (a) and after 3000 cycles (b). The relationship between the applied potential (dotted line) and corresponding amplitude (solid line) and frequency (dashed line) plots, (c) is before 3000 cycles and (d) after 3000 cycles. Arrow indicates the amplitude peak leading the applied potential by one quarter of a cycle.

have been extensively reviewed by Glab et al. [27] and have been the object of intense investigation notably by Burke et al. [24].

The increase in current in the SWV after 3000 cycles (Fig. 2(b)), compared to the SWV before 3000 cycles (Fig. 2(a)), is due to the hydrous oxide growth on the surface of the iridium electrode leading to an increase in pseudo-capacitance, which is reflected in the change in amplitude and frequency. This can be clearly seen, in Fig. 2(c) and (d), for the Hilbert amplitude (solid line) where the initially small peak (marked by arrow in Fig. 2(c) and (d)), one quarter cycle ahead of the maximum stimulating voltage (dotted line), is seen to grow dramatically following 3000 potential cycles (Fig. 2(d)). This is consistent with an increase in pseudo-capacitance

as the charge-storage capacity grows, which is associated with the growth of the hydrous film [24].

3. It is well-known that *p*-phenylenediamine causes electrode fouling at the pH used at solid electrodes [28] which has been exploited to form perm-selective or gas permeable membranes on electrochemical sensors [29]. The mechanism is initiated by the solution phase 1,4 addition of *p*-phenylenediamine to the diimine electrode oxidation product to form an electro-active dimer [30]. Further 1,4 additions leads to the formation of a compact insulating film.

The Hilbert transform of the phenylenediamine data shows a decrease in amplitude due to a change in the area of the electrode surface and an increase in the frequency (Fig. 3(b) and (c)), from the current response

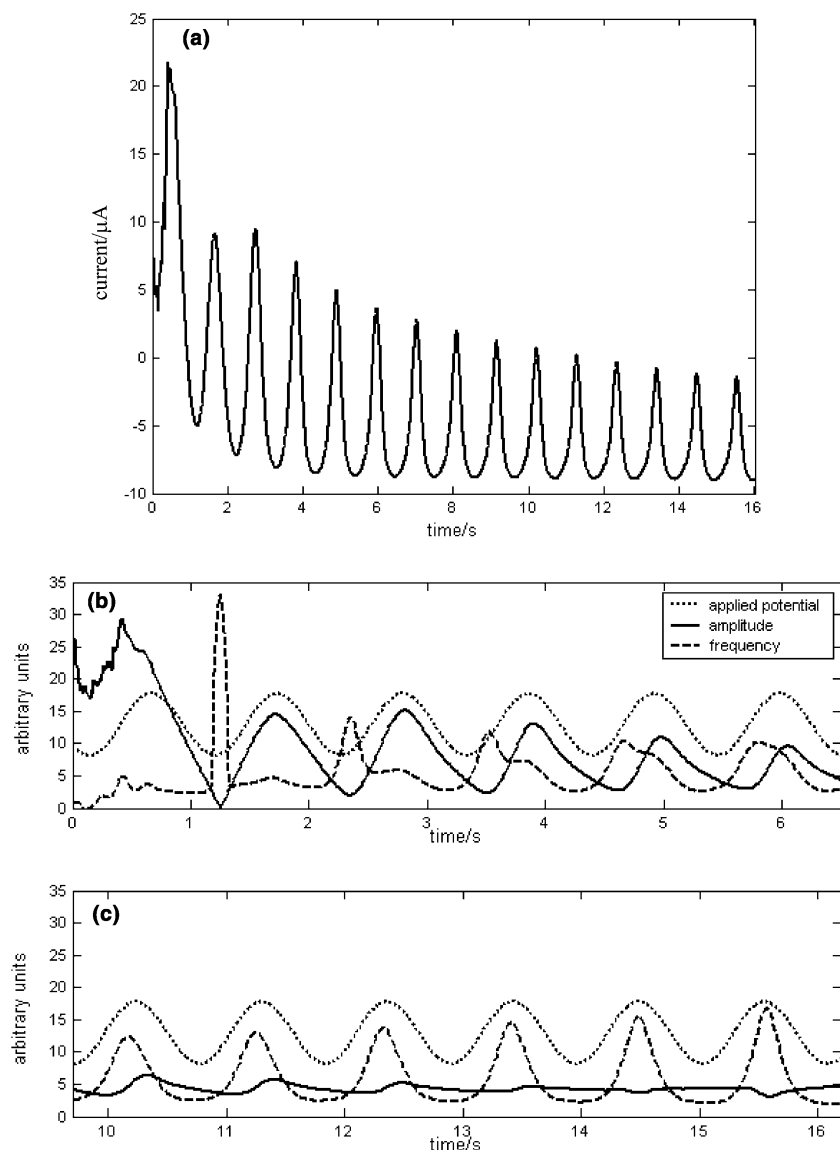


Fig. 3. Formation of a passivating layer as a result of the oxidation of 10 mM *p*-phenylenediamine on a 2 mm platinum electrode showing the output current response, in (a), and its corresponding Hilbert transform showing overlays of applied potential (dotted line), amplitude (solid line) and frequency (dashed line) (b) and (c). The frequency, in (b), has a double peak which reduces to just a single peak after approximately 6 s (c).

(Fig. 3(a)). Fig. 3(b) and (c) shows the frequency (dashed line) changing from a double peak, at the beginning of the scan, to a single peak at the end. The frequency shows three clear regions: (i) the initial cycle and then; (ii) the appearance in the second cycle of a large peak in instantaneous frequency one quarter of a cycle after the maximum stimulating voltage, which dies away in approximately 6 s (Fig. 3(b)); (iii) the slow

appearance of another peak in instantaneous frequency in phase with the maximum stimulating voltage which grows steadily (Fig. 3(c)). By the end of the trace (Fig. 3(c)), the first peak in frequency has completely disappeared but the second peak continues to grow due to the build up of a complex polymeric insulating film on the surface of the electrode. The amplitude (solid line), however, has decreased significantly, becoming

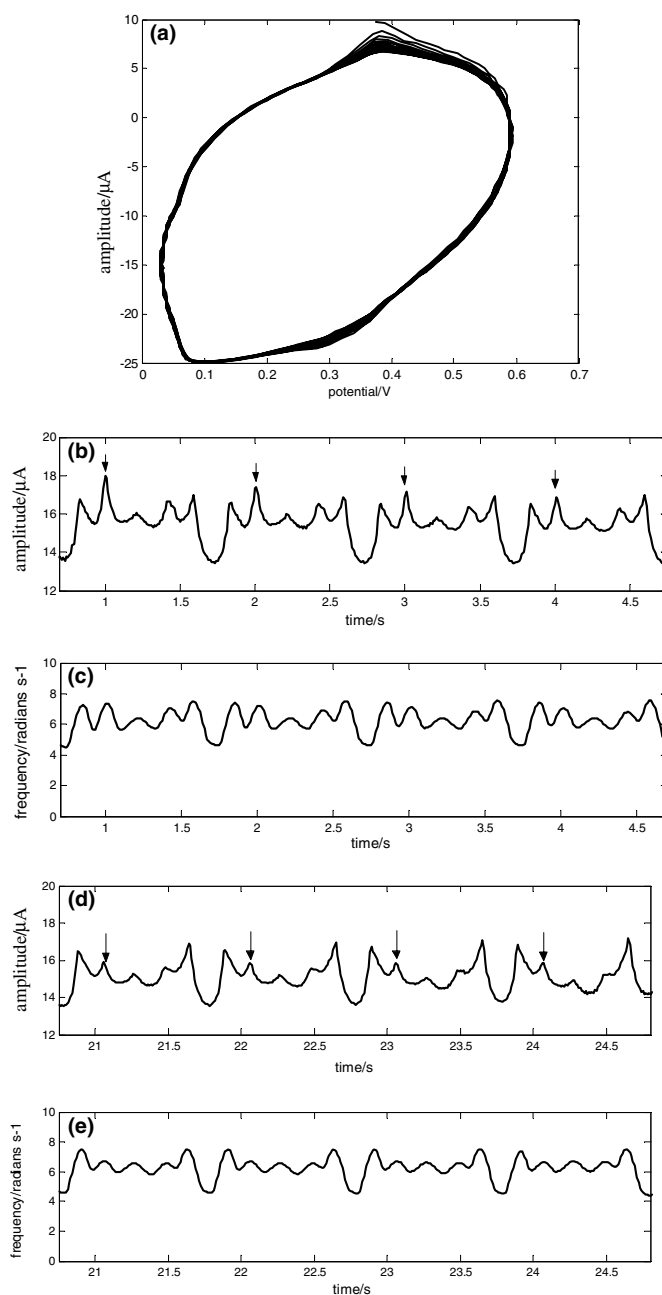


Fig. 4. Oxidation of 5-hydroxytryptamine (5-HT) showing the amplitude and frequency plots at the beginning of the sinusoidal perturbation (b) and (c) and end of the sinusoidal perturbation (d) and (e) for the 20 mM concentration of 5-HT and SWV plot (a) showing overlay of approximately 25 cycles. The change in amplitude of the oxidation peak can be seen at approximately 0.4 V from the cyclic voltammogram although it is not as obvious as the change in the arrowed oxidation peak in the amplitude plot in (b) and (d). In addition the frequency also changes which suggests a change in the rate of reaction due to adsorption of 5-HT products on the glassy carbon electrode. Therefore, the change in frequency gives an early indication of the fouling of the electrode surface.

nearly constant. None of this is visible in the largely featureless voltammogram.

2.4. 5-Hydroxytryptamine (5-HT) analysis

Fig. 4 shows the 20 mM 5-HT concentration in detail where it can be clearly seen that there is a change in amplitude and frequency due to the adsorption of 5-HT products on the surface of the glassy carbon electrode. The cyclic voltammogram, Fig. 4(a), shows a small increase in the oxidation peak (at ≈ 0.4 V). However, the change in amplitude is more obvious from simple visual inspection of the Hilbert transform (amplitude plot in Fig. 4(b) (arrowed peaks)). The frequency also changes in Fig. 4(e), compared to Fig 4(c), which is again due to a change in the electrode reaction rate. This is in sharp contrast to the thermodynamically reversible reaction of hexaammineruthenium(III)chloride where there is a change in amplitude but no change in the frequency. This, therefore, suggests that the frequency plot is a more sensitive indicator of a change in electrode reaction rate due to the effect of the adsorbed oxidation products of 5-HT on the electrode current density.

It should be noted that the fouling of the electrode due to 5-HT is flux dependent and therefore will change according to the size of the electrode. This can be seen when comparing a 30 μm electrode to a 3 mm glassy carbon electrode where the carbon fibre is affected by a lower concentration of 5-HT, 5 μM compared to 2 mM for the 3 mm electrode.

3. Conclusion

The Hilbert transform is applicable to the analysis of electrochemical processes which are intrinsically non-linear and non-stationary. The validity of the Hilbert transform to non-linear signals makes it an ideal tool for electroanalysis. From the reactions shown in the three examples it can be seen that the amplitude scales with the concentration and the frequency data is characteristic of the electrode reaction rate. The 5-HT experiment, where the change in frequency acts as an early warning system to the fouling of the electrode, highlights the advantage of using the frequency aspect of the Hilbert transform to effectively check the change in the electrode functionality, which is especially important when doing in vivo experiments. There is, therefore, a clear advantage in using the Hilbert transform where analytical and kinetic data can be extracted from the same experiment with no loss of phase data. In addition, as well as obtaining qualitative information, there is the possibility of obtaining the direct quantification of the rate constant, k (both heterogeneous and mass trans-

port) from $d\theta/dt$, which has the same dimension and corresponds to k . The frequency plot also offers advantages in high speed voltammetry (where the charging currents are high) in situations where no background subtraction is possible e.g. electrode fouling and oxidation growth.

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