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Pulse Polarography - Theory and Application

By

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1. Introduction

Classical do polarography has been used widely for chemical analysis for both inorganic and organic compounds, and has an extensive literature (1). However, do polarography is not satisfactory at concentrations below about 105M, and resolution becomes very poor in the presence of a relatively large concentration o£ a more easily reduced depolarizer. For the purposes of improvement in sensitivity and resolution, a number of variations on do polarography have been developed (2). One of the best of these variations is pulse polarography. Pulse polarography was first developed by Barker (3) as the outgrowth of his work with square wave polarography. Several general articles on pulse polarography have been published (4- 7). We present here the theory and applications of pulse polarography from an analytical point of view.

2. Theory and Instrumentation
In this section we describe the basic wave forms o£ the pulse technique
and the resulting current-time and current-potential response. Development of the basic theory allows us to relate measured current to analyte concentra-tion, the quantity of interest, and to predict how changes in experimental parameters will affect the sensitivity and detection limits of analytical methods. Because much analytical work is concerned with reductions at the dropping mercury electrode (DME), this situation is singled out for special treatment. Finally, we discuss briefly various instrument characteristics important to analytical applications.

2.1 Potential-time Impulse and Current-time Response
There are two important sources of current resulting from pulse appli-cation: the faradaic current which is proportional to the concentration of depolarizer in the solution and the capacitative current required to charge

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the electrode double layer. The main idea behind the pulse technique is that the capacitative current which flows at an electrode in response to a potential

pulse decays exponentially, while any faradaic current decays at a much slower rate. The current can be measured at some time after pulse applica-tion which is long enough so that the capacitative current is negligible while the faradaic current is still appreciable. Thus, the measured signal, the cur-rent, is much more nearly a pure faradaic current, and hence proportional to the concentration of depolarizer, than is the case with do polarography. These points have been discussed in detail by Barker and Gardner (8) and by Christie and Osteryoung (9).
Figure l a illustrates typical wave forms and measurement schemes employed in the normal pulse polarographic (NPP) and differential pulse polarographic (DPP) modes. The NPP mode employs a series of pulses, each of greater amplitude than the previous one by the same amount, so that the envelope of the potential-time (E-t) curve is a linear potential scan. In the DPP mode, the E-t curve consists of a linear potential scan on which is superimposed a series of constant amplitude pulses.

Fig. 1.
Schematic representation of poten-
tial-time and resulting current-time
curves for normal and differential

pulse polarography, a) Potential-
time waveforms; b) Same as a, expanded time scale, showing the time intervals, S t, over which current is averaged; c) Current-time curve showing the difference

current signal, a(i av).

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Figure 1b shows the E-t trace for NPP or DPP on an expanded time scale. As can be seen from the time scales in Figure 1, the scan rate in DPP is slow enough and the pulse width is narrow enough that the change in potential due to the scan during the life of the pulse is negligible.
Figure 1b also identifies the pulse amplitude, zE, and a time interval, St, over which the current is measured and averaged.

Figure 1c shows a typical i-t trace resulting from the pulse application,
and the output signal, •¢(iav) , which is the difference between the average
current measured near the end of the pulse and that measured just before
pulse application. The difference current measurement is essential to the
differential pulse mode, but is often omitted in the normal pulse mode, in
which case the signal is just the average current measured near the end of
the pulse life.

The normal pulse polarographic current-potential curve has the same shape as the do curve and many of the same features. The most important of these is that the limiting current is directly proportional to the concentration of the electroactive species and that the proportionality constant is independent of the rate of electrochemical reaction. In contrast the peak height in DPP, while proportional to analyte concentration, also depends on the electro-chemical reduction rate and therefore is sensitive to the exact matrix.

Theoretical treatments of pulse polarography include those of Barker and Gardner (8), Los and co-workers (10-16) and Parry, Osteryoung and Oldham (17-23). From the analytical point of view, the important theory of the pulse polarographic technique defines those parameters which affect the signal, the pulse polarographic current, and its relationship to concentration of the electroactive substance.

2.2 Current-concentration Relationships
Pulse polarography is applicable to a wide variety of electrode mate-
rials and geometries. In each case, the current-concentration relationship
is determined partly by the geometry, and some of the resulting equations are quite complex. We will discuss the pulse polarographic technique using
the chronoamperometric equations for the simple case of semi-infinite linear
diffusion.

2.2.1. Normal Pulse Polarography
The normal pulse current on the diffusion plateau is simply the Cot-trell current (17):

id=nFAD1/ZCb/(7rtm)'' (1)

where id is the current in microamperes (ƒÊA), n the number of equivalents
per mole, F the Faraday (96500 coulombs/equivalent), A the electrode
area in cm2, D the diffusion coefficient of the reacting species in cm2 /s,

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Cb the bulk concentration in mM, and tm the time in seconds, measured from pulse application, at which the current is measured. In Figure 1b we illustrate a time interval over which the current is averaged, while in Equa-tion 1 we refer to an instantaneous measurement time. The correct meas-

urement time, tm, to use in Equation 1 for the situation of Figure 1b would be given by :

tm1/2 =(t'1'2 +(t- t)1/2)/2

where t is the pulse width (t2 -t 1 of Figure 1b), and St the sample width. However, for the times we are interested in this is about equal to the aver-age time:

tm =t-Ot/L

Equation 1 has several important features. First, the current is directly proportional to the concentration, and none of the constants should change appreciably in value due to change in matrix. Even the diffusion coefficient, D, is relatively insensitive to changes in electrolyte composition and so on. Second, the current decreases as tm 1, This means that the measurement time should be as small as possible in order to maximize the signal. On the other hand, the measurement time must be large enough so that the capaci-tative current is negligible, and so that practical requirements of instrument design can be met. The times, tm, typically used are in the tens of milli-seconds range. A further point worth emphasis is that Equation 1 (and the more detailed equations for different geometries which follow) is remarkably accurate and therefore can be used to check the validity of an analytical procedure. If the calculated and measured currents for a known concentra-tion differ by more than about 5%, there is probably something wrong which can result in bad analyses.

2.2.2. Differential Pulse Polarography
The premise of Equation 1 is that the overpotential is sufficiently
large and that there is sufficient absence of solution chemical complications that the electrochemical reaction rate is diffusion controlled. In the dif-

ferential pulse case, we are measuring, not a constant current on a plateau

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but rather the rate at which the current increases to that plateau value as the potential is changed. Therefore we must be very careful to specify whether we are dealing with a fast (reversible) electro-chemical reaction. In the following, we will assume that the electrode reaction is fast and that there are no other chemical kinetic complications.
First let us look at the current as a function of potential for the wave
in NPP. The Nernst equation can be written as:
E = E1/2 - (1/nf)ln(Red/Ox)
=E1/2-(1/nf)ln(i/(id-i)) (2)

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where E is the potential and E1/2: the half wave potential for the reaction Ox + ne-= Red

f = F/RT where R is the gas constant (8.3 14 joules/mole-deg), T the absolute temperature (°K), i is the current at E, and the other symbols have been previously defined. Equation 2 can be rewritten as:

(3)

where

e = e+ nf(E-Ey2) (4)

Using Equation 3, one can then find the difference current, i (E + DE) - i (E) = 0i (E) (18):

di(E)/id =e(a2--1)/(Q2+E)(1+E) (5)

where a = exp (of DE/2). Note that 0E is a signed quantity; cathodic going pulses have negative sign.
The maximum value of zi (E), ii (Er) = ip, is found by differentiating Equation 5 and is given by:
1pI1d=)I(0+l) (6)
E=Ei/2-E/2 (7)

It is interesting to note that Equation 5 actually gives the derivative current, whereas the DPP experiment employs a differential current meas-urement. Agreement of theory with experiment arises from the fact that the do current contribution is small. These relationships have been experi-mentally verified by Christie and Osteryoung (24). Saito and Himeno (25) have reexamined in detail these relations using the reduction of Cd(II), Co(II). Tl(I1 and Zn(IIl.
Let us call the peak difference current in differential pulse iDpp and
the diffusion current in normal pulse iNpp. Then Equation 6 can be rewritten as:

iDWiNPP(al)/(H) (8)

The ratio (a-1) / (a + 1) depends only on the number of electrons transfer-red and on pulse amplitude, DE, and is always less than one. Table 1 and Figure 3 show values of the ratio as a function of ZE for various values of n. It can be shown through a simple diffusion layer argument that in the absence of complicating kinetic factors Equation 8 always applies, regard-less of electrode geometry. Therefore, the procedure for calculating the DPP current is to calculate the NPP current and apply Equation 8.
For small values of the pulse amplitude, the ratio of Equation 8 can
be approximated by:

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Fig. 2. Variation of (o -1)/(o + 1) = iDpp/iNpp with pulse
amplitude •¢E, for various values of n .

Table 1 Values of (a 1)/ (a+1) for various values of DE and n.

(a-1)/(a+1)=nfE/4 .(9)

For small pulse ampitudes the DPP current increases roughly linearly with pulse amplitude, and therefore an increase in 0E gives better sensitivity. However, as can be seen in Figure 3, at larger pulse amplitudes the relative increase in current obtained by increasing LE is less. In practice, the opti-mum pulse amplitudes to maximize sensitivity lie in the range 50-100 my. Larger pulse amplitudes are not useful in part because of the problems with residual capacity currents (see below) which are aggravated at larger pulse

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amplitudes.
Equation 9 also shows that the ratio increases linearly with n. Since
iNpp increases linearly with n, for small pulse amplitudes iDpp increases linearly with n2. This suggests the special usefulness of DPP analysis for certain organics and oxyanions in which the number of electrons transferred is large. A three-electron reaction has 9 times the sensitivity of a one-electron reaction, and so on.

The attractive analytical features of the differential pulse current have
to be balanced by the observation that there are often kinetic complications which cause the current to be less than that predicted by Equation 8. Although peak current is always proportional to concentration, the constant of proportionality depends on the rate of the reaction. Minor changes in matrix from sample to sample can cause major changes in reaction rates, and therefore major changes in the peak height-concentration ratio. In developing a method for a specific sample type, it is always wise to measure iDpp and iNpp and compare their ratio with that predicted by Equation 8. If the two differ by more than about 5%, one should be prepared for trouble if there is any variation in sample matrix. If the electrochemical reaction rate of the substance sought is slow, even a small change in matrix, which may be impossible to anticipate or detect, can lead to substantial changes in reaction rate, and hence substantial changes in the current/concentration ratio.

2.3. Resolution

Electrochemical methods of analysis frequently can be used to analyze
a sample for several species simultaneously. Therefore the question of resolu-tion and its relationship to sensitivity is important to pulse polarography. The problem of resolution of do polarographic waves has been worked out
(26) and applies with appropriate modification to the NPP case. We won't discuss that here, but will deal with the DPP case. Let us first consider the peak resolution at small pulse amplitudes.
The peak shape can be described for small pulse amplitudes by dif-ferentiating Equation 3:

i(E)/id =nfeL\E/(1+e)2 (10)

To define the peak half width, Wye, we wish to find the potentials at which the current is equal to half the peak current. To do this, we set 1/2 of the rhs of Equation 9 equal to the rhs of Equation 10:

of OE/8 = nfe•¢E/(1+ƒÃ)z

The solution is (8)

E= 3 •¬or Wy2 =E+-E- = 3.52/nf (11)

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Equation 11 says that for small pulse amplitudes the peak width is indepen-dent of pulse amplitude and inversely proportional to the number of electrons transferred. Wl is equal to about 90, 45, and 30 my, for n = 1, 2, and 3, respectively, at room temperature (18, 27).
The equation for W1 at larger pulse amplitudes depends on pulse ampli-
tude and is more complicated:

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The variation of Wl with ZE for various values of n is shown in Figure 3. Notice that the peak is narrower, but broadens more rapidly with increasing a E, for larger values of n. Also notice that for all values of n the peak width approaches the pulse amplitude for large pulse amplitudes.

Fig. 3. Variation of peak half width, W1, with pulse amplitude

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DE, for various values of n.

To get some feeling for the tradeoff between resolution and sensitivity
it is useful to compare Figures 2 and 3. First, for pulse amplitudes above about 100 my the resolution gets steadily worse, but there is not much increase in sensitivity. Therefore, even in the absence of complicating factors there is no point in going to pulse amplitudes larger than this. Second, for pulse amplitudes below about 20 my the sensitivity increases rapidly with

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increasing pulse amplitude, but the resolution is relatively insensitive to
change in pulse amplitude. Therefore, there is no point in using pulse ampli-
tudes smaller than about 2ƒÆ my. In the intermediate range increasing pulse
amplitude improves sensitivity but degrades° resolution, so DE should be
chosen according to the demands of the individual sample.

2.4. Pulse Polarography at the Dropping Mercury Electrode
When pulse polarography is used at the DME, the droptime is usually
controlled mechanically and set at some fixed time less than the natural
drop time. The potential-time wave form is synchronized with the beginning of the drop life so that a pulse is applied at the same time in the life of each drop. For example, if a two second drop time were used, a pulse might be applied at 1.94 s on each drop.
For NPP at the DME Equation 1 should be replaced by:

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where iNPP is the average current, ti is the time in the drop lice at which
the pulse is applied, ƒÆ"=(z - t1) / t 1 where r is the drop time in seconds,
and t 1 (ƒÆ" - ƒÆ') is the time period over which the current is averaged.
A and B are functions of time given by:

A = ((1+ƒÆ")'- 7/3 1)1/2 - ((1+ƒÆ')- 7/3-1)1

B =1.1 t11/6 ((1+ƒÆ")7/3- 3 (1+ƒÆ')7/3) (14)

Equation 13 is intended for use with an ordinary blunt end DME capillary and under routine conditions should be accurate to a few percent. The equation has been developed and experimentally verified by Fonds et al. (11). It should be pointed out that the NPP experiment is a "first drop" experiment. That is, the starting potential is usually one at which the only reaction occurring is the reoxidation of the substance reduced during the pulse. Therefore there is no depletion effect, and Equation 13 should give good values for diffusion coefficients (11, 28).
The sensitivity of NPP with respect to do polarography can readily
be calculated by returning to Equation 1, substituting the appropriate area term for the growing drop, and including the factor (7/3)1/2 of the Ilkovic Equation:

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For reasonable values of td and tm this ratio lies in the range 3-6.
Of course, the NPP detection limits are lower than 1/3 to 1/6 of the DC

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values because the detection limits depend on the capacitative background current as well as on sensitivity.

2.5. Capacity Currents at the DME
The dropping mercury electrode is generally the most satisfactory electrode for working at cathodic potentials. Mercury electrodes are easier to use than solid electrodes because of the reproducibility of the liquid surface. The DME also has advantages of reproducibility and freedom from artifacts over the hanging mercury drop electrode (HMDE). The DME, however, exhibits a residual do capacity current which arises from the change in electrode area with time and which must be taken into account in analytical applications of NPP and DPP (9, 29, 30).
At each potential, the electrode surface must have a certain charge density determined by the capacity of the electrode. The total charge re-quired depends on the potential and on the area of the electrode. Referring back to Figure 1, at time t 1 the electrode might have potential E1 and area A1. At time t2 the potential has been changed to E2 = E1 + DE, and the area has increased to A2. The difference in surface charge, OQ, under these two conditions, is

OQ - Q(EZ,AZ)-Q(Ei,Ai) (18)

The current that flows to supply this charge difference is the do capacity current. This current is roughly proportional to . where r is the drop time, so the capacity current is decreased by working at longer drop times. Also, the capacity current is relatively insensitive to the pulse width while the faradaic current is relatively insensitive to the drop time over the usual range of choices of these parameters. Therefore, the faradaic current is always enhanced relative to the capacitative current by working at narrower pulse widths and longer drop times. In order to obtain reasonable instru-ment performance and definition of the experimental curves, it is necessary to use potential scan rates which do not produce changes of more than a few millivolts during the life of each drop. Therefore longer drop times require slower scan rates and lengthened analysis times. The tendency is to work at the shortest drop times and fastest scan rates possible (say 0.5s, 10 my/s) in order to minimize the time. However, under demanding condi-tions detection limits can be substantially improved by increasing the drop time and decreasing the scan rate (say to 5 s,1 my/s).
In NPP each pulse has greater amplitude than the previous one and during the course of the scan the pulses become quite large. This results in a steeply sloping baseline which is the main limitation on detection limit. For a two electron reaction, ordinary do polarography is capable of detec-tion limits in the range o£ a few micromoles per liter (ca 200 ppb). NPP, on the other hand, is capable of detection limits lower than this by about

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a factor of 10 (0.2-0.4 ƒÊ1V1 or 20-40 ppb).

In DPP, each pulse has the same amplitude, which tends to decrease
the problem of the capacitative background current. Also, although the faradaic response decreases with decreasing pulse amplitude, in the inter-mediate range of pulse amplitudes in some solutions the capacitative cur-rent will decrease more, so that detection limits are actually improved by decreasing the pulse amplitude (9, 24). The lower capacity current in the DPP mode permits detection limits in the 20 nM range to be attained, that is, about ten times lower than NPP.
The current-potential capacitative background curve in NPP resembles
an integral capacity curve and is very nearly linear (31, 32). The correspond-ing curve in DPP, though smaller in magnitude, resembles the differential capacity curve, and therefore, typically has a good deal of structure (31, 32). A background curve with structure can cause substantial analytical problems. Consider first the dependence of the shape of the background curve
on the nature of the solution. High salt concentrations tend to produce a relatively flat background in DPP, and as the salt concentration is decreased humps and bumps become more pronounced (31, 32). The point has often been made that in order to avoid migration currents only a hundred fold excess or so of indifferent electrolyte is required, and that the conductivity requirements of the solution for DPP are not demanding (33). Therefore in principle one can carry out trace metal analyses in the presence of very low supporting electrolyte concentrations. In particular, many natural waters should be directly analyzable without addition of supporting electro-lyte. However, at low salt concentrations the background current may be unsatisfactory because of its structure, and may undergo unanticipated change due to change in the salt concentration. Therefore, in the absence of compelling arguments for doing otherwise, one should use a high (>ca 0.01M) and uniform salt concentration by adding supporting electrolyte to attain a reproducible and relatively flat background current.

A further problem with the capacitative background is that minute
amounts of surfactants can produce peaks in DPP at the potentials where
they are adsorbed on the electrode surface (3.0). These peaks are often
hard to distinguish from those due to electroactive substances and are likely
to occur in natural samples. Consider the illustration in Figure 4. Curve 1
shows the background current in the supporting electrolyte solution. Curve
2 shows the peak resulting if the solution is made ƒÊM in Cu(II) (64 ppb).
This situation would permit a good analysis for Cu(II). Curve 3 shows the
effect on the capacitative background of making the supporting electrolyte
0.001% in Triton X-100, a commonly used surfactant amd maximum supres-
sor. Curve 4 shows the combined effect of Triton X-100 and Cu(II). There
is no reasonable way to analyze curve 4 to find out how much Cu(II) is
present. Under these conditions, the standard addition method could not

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Fig. 4. Illustration of capacitative background current problems in
DPP. Curve 1: •¢.E = +25 my (anodic going pulses), scan
direction - anodic; drop time = 2 s; scan rate = 0.5 my/s,
m = 1.23 mg Hg/s; 0.1M KNO3 + 0.1M HOAc. Curve 2:
Same as 1, but 1 ƒÊM in Cu(II); Curve 3: Same as 1, but
0.001% in Triton X-100. Curve 4: Same as 1, but 1 ƒÊM in
Cu(II) and 0.001% in Triton X-100.

be used, for it also depends on accurate background correction. However, there are other tactics which may be used. Amperometric titration with DPP endpoint detection is often a suitable alternative which avoids the back-

ground problem (30). The supporting electrolyte may be changed to change both the capacitative current characteristics and the peak position for the species of interest. The Cu(II) reduction wave can be changed over one volt in position by changing the complexing characteristics of the medium. It is highly unlikely that duplicate determinations of a sample in greatly different media giving the same results would both include the same back-

ground correction error.
These problems do not occur, of course, for sample types in which
the background current can be determined directly. For example, analysis of sediments for heavy metals might employ an acid digestion which produces a uniform sample type with a background indistinguishable from that due
to the digestion medium. Extraction and chromatographic procedures for
sample cleanup also tend to produce uniform and determinable capacita-tive backgrounds.

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2.6. Instrumentation

There are now several commercial instruments to do pulse polarography
in at least one mode produced by Princeton Applied Research Corporation, Tacussel Solea, and Brinkmann Instruments. ` Pulse polarographs were also at one time produced by Southern Analytical, Ltd. and by Melabs. The only presently available instruments which provide both NPP and DPP modes are those of PARC and Tacussel. The Tacussel PRG-5 and PARC 174 are low cost instruments designed for analytical use while the Tacussel PRG-4 com-bined with a suitable potentiostat (e.g. the Tacussel 30-01) and the PARC 170 are more expensive instruments which provide greater flexibility. The Tacus-sel instruments are more difficult to maintain but have the advantage of more operator choice in the selection of instrumental parameters.
Recently, Osteryoung et al. have developed some new pulse polarogra-phic techniques designed to minimize the do capacitative background resulting from drop growth. The effect of this capacitative component may be reduced by making only one measurement on each drop, always at the same potential and at the same time in the drop life and applying a pulse only on alternate drops. This technique, called alternate drop pulse polarography, is described in detail and experimentally verified by Christie et al. (34). Another tech-nique for dealing with background current is called constant potential pulse polarography, in which the value of EZ as shown in Figure 1(b) is the same for all drops (35). Only one current measurement is made per drop at poten-tial EZ and time ti (1+8°); the output current as a function of E1 is of the same form as a normal pulse polarogram. An additional virtue of this technique is that it can be carried out using a commercially available instrument, the PARC Model 174, with only a minor modification (36). Klein and Yarnitzky
(37) also have examined various alternative schemes for current sampling to increase the sensitivity and lower the capacitative background current in pulse polarography.
Vassos and Osteryoung (38) have made a low noise digital pulse polaro-graph suited for both manual and computer controlled operation. In this instrument, the use of integrated circuit techniques and two drop operation provide an output effectively free of noise and background, and without peak distortion. Computer control provides the flexibility of determination of experimental parameters through software.
Los et al. (39) have also made a new pulse polarograph for normal mode instantaneous current sampling with digital circuitry to control timing and potential generation. In this instrument pulse times and delay times are independently variable over a wide range. Los et al. (40) applied this instru-ment to measurement of proton diffusion in aqueous sulfate solution.
Abel et al. (36) have modified a commercial instrument, the PARC 174, to permit variation of the current integrator time constant, the sampling time, and the drop time or sampling frequency. The resulting flexibility is

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advantageous for optimization of methods and for minimizing distortion due to long integrator time constant (41).

3. Analytical Applications

In this section we survey some representative work of analytical impor-tance employing pulse polarography. It is a testimonial to the widespread application of these techniques that it is no longer practically possible to compile all of the literature, for many papers which report results obtained using pulse polarography mention the technique only in passing and are never indexed by that subject heading. This section is divided into two major subsections; the first deals with direct methods and the second with anodic stripping methods.

3.1. Direct Methods

The direct methods of analysis are loosely grouped into two broad categories, inorganic compounds and organic compounds.

3.1.1. Inorganic Compounds
Since the preliminary evaluation of pulse polarography by Parry and Osteryoung (17), many applications to analytical problems have been published. The growth of applications has been especially pronounced following the introduction of inexpensive commercial instrumentation. Barker and Bolzan (42) showed that the specific adsorption of lead
ion from perchloric acid solutions is markedly influenced by the presence of bromide ions in the solution. This specific adsorption changes the shape and size of the lead waves observed in the normal pulse mode but not in the classical do mode. This is an important observation, for phenomena which change the shape of the normal pulse wave can change the amplitude of the differential pulse current. The effect of anion induced adsorption on DPP currents has been investigated by Anson et al. (43) and this predic-tion verified.

Temmerman and Verbeek (44, 45) determined traces of bismuth, copper
and lead, and nickel, zinc, cobalt and manganese in cadmium by DPP. Demerie et al. (46) employed DPP for determination of trace amounts of gallium in high-purity arsenic compounds. The detection limit was 2 X 10 8 M in 6.5M sodium perchlorate and 0.5M sodium thiocyanate at pH 2. (Note: Most workers are regretably vague and imprecise in defining the term detection limit. Here we simply quote the results with the warning that many of the numbers quoted are not based on sound statistical evaluation of adequate data, and are as a result overly optimistic.) Their procedure allowed the determination of as low as 30 ng gallium in a 1 g sample; however it was necessary to eliminate most of the arsenic matrix by a prior distillation as arsenic(III) chloride or arsenic(V) bromide due to the interference of arsenic.

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Also Lagrou and Verbeek (47) succeeded in trace-determination of
copper, lead and cadmium in cobalt without separation using DPP. The
detection limits are respectively 0.02, 0.04 and 0.1 ƒÊg in 1 g metallic cobalt
when preparing a 2 M cobalt solution by dissolving to cobalt compound in 0.1M hydrochloric acid. This corresponds to solutions 4 •~ 10M, 2 •~ 108M, and 1 •~ 107M, respectively, in the elements sought.

Galan et al. (48) determined traces of impurities (Cu, Pb, Cd, Zn, Mn, Mg, Sr and Ba) in high-purity sodium chloride by DPP and flame spectro-metry.
Leveque (49) studied the electrochemical behavior of lanthanides in N, N-dimethyl formamide. DPP procedures were found to be especiall useful for analysis of mixtures containing a Yb-rare earth. The lanthanide cations were reduced in two steps with the formation of amalgams. The Ce-rare eaths were reduced in one step only with formation of amalgams. Recently Fawcett
(50) applied DPP to determination of uranium in plutonium-238 metal and oxide, in which the highly a-active isotope, 238Pu, is important to use as a source of thermal energy for power in space and for human heat pacers. O'Deen and Osteryoung (51) employed NPP to study the electrochemi-
cal behavior of halide ions in molten nitrates and concluded that the electrode

process is a reversible one-electron formation of a soluble product. They demonstrated the value of NPP in cases such as depolarization of mercury to form an insoluble product in which film formation phenomena render the do mode useless (see below ref 68). Garber and Wilson (51) applied DPP to determination of sulfur dioxide at low concentrations in air. The

procedure outlined is a simple, fast and sensitive method for the determin-ation of atmospheric sulfur dioxide down to 0.1 ppm sulfur dioxide in air (i.e., 0.7 - 0.5 µM in the polarographic solution). The sulfur dioxide was absorbed into solution by bubbling the air sample through dimethyl sulfoxide containing 0.1M lithium chloride as supporting electrolyte. After deaeration, the DPP peak current due to the reduction of sulfur dioxide was measured between -0.7 and -0.8 volt vs. Ag/AgCI. This method is free from inter-ferences from sulfide and sulfates at the 5 X 107M level with an accuracy of 25%.
Parry and Anderson (53) reported a form of pulse polarography which could be used for automated analysis of process streams containing ferric, ferrous and cupric ions. The electrochemical basis for the technique is the irreversibility of the Fe(II)/Fe(III) system under the experimental conditions. This allows one to sit at a rest potential where no reaction occurs and to pulse alternately to potentials on the diffusion plateaus for Fe(II) oxidation and Fe(III) reduction. This technique is rapid, i.e., the analysis is performed by the application of a single 50 msec pulse to the diffusion plasteau of the analyte, and is not severely affected by small amounts of oxygen. This tech-nique was useful for monitoring a copper etching bath.

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In the area of environmental pollutants, Cox (54) reported advances
in polarographic techniques applied to environmental monitoring, discus-sing several metal cations of toxicological importance. Myers and Osteryoung
(55) studied the determination of arsenic(III) at the parts-per-billion level in several kinds of supporting electrolyte; 1M HCl was found to be the most suitable. Satisfactory procedures for common intereferences were developed. The detection limit is 3 X 109M at the 95% confidence level. Myers et al.
(56) also carried out successful arsenite determination in the presence of microorganisms. Heckner (57) applied pulse polarography to simultaneous determination of arsenic and lead in water and aqueous spoil extract by proper choice of supporting electrolyte to separate the waves. Detection limits for arsenic were almost the same as reference (55). Reinke et al. (58) determined arsenite and arsenate ions in fish and shellfish by selective extrac-tion and DPP.
Gadde and Laitinen (59) studied interaction of lead with corn root exudate by NPP.

Myers and Osteryoung (30) applied pulse polarography to amperometric
titration. This technique has the merit of being independent of do capacita-
tive current contributions. They could titrate copper ion by EDTA with
adequate precision and accuracy at the 107M level. However, they pointed
out the serious problem of adsorption of metal cations on the cell walls at
trace levels in near neutral solution. Roux et al. (60) determined tellurium
(IV) over a concentration range of 2 X 109 - 2.4 •~ 10 $ M in HCI-NaCI
without interference by 10 5 - 104M bismuth. Goldberg and Parry (61)
applied pulse polarography to the determination of the apparent oxidation
state of metal dissolution in a titanium-aqueous sulfuric acid system. Claus
(62) determined the rate constant, k, of the oxidation of Ti(III) by NH3OH+
ions in oxalic acid by using pulse polarography.

Bolzan (28) tested NPP for the measurement of diffusion coefficient
of cadmium ion in various supporting electrolytes of different concentrations. He pointed out that the viscous effect, ion-pair formation and complexation must be taken into account in different degrees of importance to explain the values of D in each medium. Saito and Himeno (63) discussed the Ni(II) reduction wave in unbuffered medium containing dissolved oxygen; the normal pulse polarogram showed a two-step reduction wave, whereas the corresponding sampled do polarogram exhibited a single wave. They con-cluded that Ni(II) is reduced at the potential where the first wave is observed and the second wave is due to the reduction of Ni(OH)2 formed by the reaction between Ni(II) and OH-arising from oxygen reduction. The same authors (64) investigated the anomalous waves observed in NPP in solutions
containing methylene blue, bisdiethylthiocarbamyl-disulfide, CuSCN and
zinc ion. The effect of pulse-polarity (the sign of the pulse amplitude) on the shape of normal and differential pulse polarograms was studied by Kaplan

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and Sevastyanova (65). They found two waves in normal anodic pulse polaro-

grams in the case of irreversible reductions, for e•~ample, a second wave on
the anodic NPP of Zn(II) in ammonia-ammonium chloride. The dependence
of the peak height in DPP, with anodic and cathodic pulses, on pulse ampli-
tude, drop time, and measurement time was also discussed.
Crosmun and Mueller (66) undertook the determination of Cr(VI) in
natural water using DPP. They were able to determine 9.6 •~ 107M Cr(VI)
in the presence of 9.7 •~ 106M Cu(II) and 10 5 M Fe(III) without interfer-
ence. The natural water samples contained from 7 •~ 10' -- 4 •~ 105 M Cr
(VI) and the detection limit was 1.9 •~ 107M. Abdullah and Royle (67) also
studied the determination of copper, lead, cadmium, nickel, zinc and cobalt
in natural water, after their preconcentration on chelating resin in its calcium
form. The metals were determined in the same sample in groups by employ-
ing first an HCl medium for Cu, Pb, and Cd, adding NH3 for the determina-
tion of Ni and Zn, and finally dimethylglyoXime for Co. Standard additions
were used to quantify the results. Solutions as analyzed had concentrations
of appro•~imately 6, 2, 3, 6, 60, 0.6 •~ 10$ M, respectively.
Turner et al. (68) used NPP for the determination of two anions, sulfide
and iodide, which lead to insoluble products at a mercury electrode. This is
possible using the normal pulse mode, in contrast with the differential pulse
or classical do mode, because there is less film formation. The detection
limits for sulfide and iodide ion were 3.5 •~ 107M and 9.4 •~ 107M, respec-
tively (see below ref 88).

Herring and Liss (69) determined iodate and total iodine in seawater, after minimal chemical processing, by DPP.

3.1.2. Organic Compounds
Wolff and Nurnberg (70) used DPP for micro and trace analysis for
aromatic nitrocompounds. Under suitable experimental conditions, the
detection limit may go down to 0.5 ƒÊg/Q (3.6 •~ 109M) for some of the
nitro-compounds studied. They also discussed the resolution and the tole-
rable e•~cess ratios for the determination of the isomeric nitroanilines.
Lal and Bauer (71) applied pulse polarography to the investigation
of lead-tropolon comple•~es.
De Silva and co-workers (72, 73) have applied DPP to pharmaceutical
chemistry and developed procedures for the determination of glibornuride
(a tolylsulfonyl urea hypoglycemic agent) and 2, 4-diamino-5-(3, 4, 5-
trimethoxybenzyl)pyrimidine (trimethoprim) in blood and urine samples.
These involve the selective extraction of the compound from whole blood
or urine sample buffered to the desirable pH into some organic solvent and
then back-extraction. Following suitable clean-up of the sample, the com-
pound was determined. The detection limits on glibornuride and trimetho-
prim were 0.05 - 0.10 ƒÊg and 0.5 - 0.75 ƒÊg per ml blood or urine, respec-

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tively (5 X 108M and 4 X 107M in the solutions as analyzed).
Furthermore, flurazepam and its major blood metabolites were deter-mined in the plasma of beagle dogs and rhesus monkeys by Clifford et al. (74). The detection limit was 10-20 ng flurazepam per ml plasma. Brooks and co-workers (75, 76) studied the determination of 1,4-benzodiazopine derivatives structurally related to medazepam, chloridazepoxide and N-dimethyldiazepam, on the trace level, and also reported the trace level deter-mination of N-disalkylflurazepam and bromazepam.

Jacobsen et al. (77) applied DPP to determine diazepam ("Valium",
"Vival"
, "Stesolid"; a psychotherapeutic agent) in serum. The detection
limit is ca. 1 •~ 108M in the polarographic solution of 0.1M H2 SO4. The
determination of 2-hydroxynicotinic acid and its metabolite (78) and tri-
methoprim and its N-oxide metabolites (79) in blood and urine by DPP
were discussed.
Brooks et al. (80) developed procedures for the determination of
phenobarbital and diphenyl hydantoin in blood by DPP. The detection
limit is 4 8 •~ 106M in blood for both compounds.

Prue et al. (81) also demonstrated the potential for application of

pulse polarography to pharmaceutical chemistry: they reported the deter-mination of disulfiram (Antabuse) which has been used for the treatment of alcoholism. The overall reaction is as follows:

(C2H5)2 NCSS2CSN(C2H5)2+ Hg -+ (C2H5)2 NCSSHgSCSN(C2Hs)2
+2e

2(C2H5)2NCSS-+Hg 2

An aqueous, ethanolic acetate buffer is used for the determination o£ disul-
firam without interference of diethyldithio carbamate. The detection limit
is 1.7 ƒÊM.

Eberle et al. (82, 83) proposed a new method for the determination
of organic pollutants, especially lignosulfonic and humic acid, in water; however, before the acids could be determined by DPP, they had to be converted to the nitroso derivatives. Other organics could be determined in the same manner as ligninsulfonic acid. The detection limit for both acids is about 5 mg/Q.
Kerchove and Patriarche (84) studied the reduction mechanism of three triiodide derivatives of benzoic acid in acidic, neutral and alkaline medium by DPP. They discussed the selectivity of the method, and compared the resolution with that of conventional do polarography.

Gilbert (85) studied the Co(II)-activated catalytic hydrogen wave
of cystine in an ammoniacal electrolyte by DPP. The detection limit
in pure solution is 5 •~ 1T8 M with 10 my pulse amplitude.

Kehr (86) applied pulse polarography to study the Brdicka protein wave of metallothionein, a cadmium-induced protein. As little as 200 ng of metallothionein could be assayed by this method.

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Palecek (87) studied polarographic characteristics of double-helical and thermally denatured DNA. It was found that the wave height o£ double-helical DNA in NPP was dependent on intial potential; in the potential range around -1.2 v the wave was more than doubled but the wave height of dena-tured DNA was almost independent of initial potential. Palecek concluded that as a result of the interaction of the double-helical DNA with the elec-

trode surface in the vicinity of -1.2 volt, DNA conformation is disturbed and some reduction sites are released for the electrode process.
Peter and Rosset (88) developed a DPP method for thiol determination. A single peak which is proportional to concentration appears when the concentration of thiol is less than 104M. The detection limit is about 107M

thiol. The overall reaction involves oxidation of mercury in the presence of the thiol with adsorption of the mercury thiolate on the electrode. They found that the method is more sensitive with a negative pulse than a positive pulse because the mercury thiolate formed during the drop life is reducible. However, the electrochemical phenomena were complicated for the con-centrations more than 104M.
Hasebe and Osteryoung (89) studied the determination of some carcino-

genic and nonvolatile N-nitrosamines, N-nitrosopyrrolidine, N-nitrosoproline
and N-nitroso-4-hydroxyproline, by using DPP. They were able to determine
8 •~ 108M N-nitrosamine under optimum conditions. Smyth et al. (90)
studied some C- and N-nitroso compounds by pulse polarographic and spec-
trometric methods. Chang and Harrington (91) also used the DPP to deter-
mine volatile and nonvolatile N-nitrosamines, N-dimethylnitrosamine and
N-nitrosoproline.

Kadish and Spiehler (92) studied the determination of digoxin and digitoxin, commonly prescribed medications. This method is suitable for direct, simple and sensitive determination for pharmaceutical products for 5 X 10 4 to 2.5 X 106M digoxin and digitoxin. Michielli and Downing
(93) determined nicarbazine, the drug for prevention of coccidiosis, in chicken tissue by DPP.

Lindguist and Farroha (94) studied the application of DPP to the assay
of vitamins, i.e., vitamin B2, nicotinic acid, nicotinamide, ascorbic acid,
and vitamins K1 and K3. The detection limits for the different vitamins

were approximately 0.01 to 1 ƒÊg/ml (8 •~ 10-8 - 3 •~ 106 M) .
Siegman and co-workers (95, 96) reported the detection and quanti-
tation of antibiotics, such as tetracycline hydrochloride, streptomycin,
penicillin G and so on using DPP. They could determine the parts-per-
million or sub-parts-per-million levels of the antibiotics which generally
exhibited very well-defined peaks with few complications in aqueous elec-
trolytes. Detection limits were about 5 •~ 10-7 M. Siegman et al. concluded
that the scope of the technique should make it useful for potency, shelf
life, and quality-control determination for antibiotics.

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Zuman (97) discussed the use of polarography for attacking practical
and theoretical problems, and reviewed the use of DPP for some organic and inorganic compounds.

3.2. Stripping Methods
It has long been recognized that pulse polarography is an elegant analyti-
cal method for discriminating against double layer charging current, while linear scan voltammetry measures the sum of the faradaic and capacitative currents. Osteryoung and Christie (98) expected that pulsed stripping voltam-metry would exhibit a lower detection limits than linear scan stripping voltammetry because of the greater discrimination against capacitative cur-rent. They also recognized the further advantage that pulsed stripping is a repetitive technique; some of the material stripped from the electrode during the pulse is replated into the electrode in the waiting time between pulses. The same material is seen many times in the pulsed stripping experiment, but only once in the linear scan stripping method.
The same authors (98) have defined the approximate theory of pulsed stripping voltammetry at the thin film mercury electrode (TFME). Oster-young et al. (99) studied the effect of supporting electrolyte concentra-tion in anodic stripping pulsed voltammetry (ASPV) at the TFME. They concluded that the response depends strongly on the resistance of the test solution, which may not be under the analyst's control unless he adds suf-ficient supporting electrolyte to remove the effects of the variable amount of electrolyte naturally present in his sample.
Naumann (100) studied the application of pulse polarography to anodic stripping from a HMDE. He was able to determine copper, lead, cadmium and zinc at the 109M level in routine work. Copeland et al. (101) used a TFME for ASPV of lead and cadmium in a variety of samples. They pointed out that the method is more sensitive than linear scan stripping techniques by factors ranging from 4 to 20 or more and also that the TFME is superior to the HMDE because of the larger ratio of surface area to volume of mercury. Batley and Florence (102) have compared the HMDE and TFME when applied to the determination of trace metals in environmental samples using several techniques of voltammetry.

Herbeuval et al. (103) also reported biological and toxicological analysis
for lead and cadmium in blood and urine with ASPV. Cornell and Pallansch
(104) determined the trace amounts of cadmium in milk by ASPV with
HMDE. Csejka et al. (105) studied the determination of the sodium salt of
2-mercaptopyridine-N-oxide by cathodic stripping pulsed voltammetry with
HMDE. This technique also could be used to determine other mercaptans.
The detection limit was ca. 8 •~ 10-10M. Forsberg et al. (106) investigated
determination of arsenic by ASV and ASPV. The detection limit of both
ASV and ASPV was 3 •~ 1010M under the experimental condition of 1M

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solutions of either hydrochloric and perchloric acid. Gold was found to be superior to platinum as a working electrode. Andrews et al. (107) used ASPV with a rotating gold disc electrode to determine the trace amounts of mercury (II) in 0.1M perchloric acid. Anderson and Tallmann (108) used a graphite epoxy TFME as working electrode.

4. Conclusions

Based on the work surveyed here we can conclude that pulse polaro-graphy has certainly come of age as an analytical technique. Perhaps the most outstanding accomplishments are those involving applications of DPP to pharmaceutical analysis and ASPV to determination of metals at ultratrace levels. We can expect work in these areas to continue at a vigorous pace as experience gained with the substrates and compounds examined is applied to related problems. The large body of work in these areas is reinforced by widespread applications of pulse polarography to problems as diverse as analysis of sea water for iodate and tissues for drugs. In more and more applications, pulse polarography is now considered a routine tool of the investigator along with chromatographic and spectroscopic techniques, and is no longer used exclusively, or even predominently, by electroanalytical chemists.

Work should be continued to develop the potential utility of pulse polarography in several areas. There is substantial room for improvement in our basic understanding of pulse polarography, especially in the differential mode. Improved understanding could lead to better choice of various time and potential parameters which determine sensitivity. Our poor understand-ing of the effects of kinetic and adsorption complications on peak heights in DPP limits our power to apply DPP, especially for analysis of organics. Thus fundamental studies should be pursued to enhance analytical utility. Better understanding of the fundamentals of pulse polarography could also provide

guides to further advanced commercial instrument design. Finally, the use of pulse polarography is limited for the analyst by the availability of reliable, well-tested methods. It is hoped that reviews such as this can stimulate method development work in all areas of application.

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