Determination of Picloram and Dowco 290 by Pulse Polarography

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The herbicide 4-amino-3,5,6-trichloropicolinic acid (picloram) and the related experimental compound 3,6-dichloropicolinic acid (Dowco 290) display reduction waves in acidic aqueous solution which provide the basis for the direct determination of these compounds. Study of the electrochemical characteristics indicates the optimum conditions are 0.1 F aqueous sulfate buffer, pH 1.9, 1% 2-ethoxyethanol (2EE), and 0.5 F H_2SO_4, 5% 2EE, respectively. Detection limits are ca. 10^{-7} M (ca. 15 ng/mL) using differential pulse polarography and calibration curves are linear up to ca. 5×10^{-4} M.

The herbicide picloram is widely used in agriculture, mainly for the control of woody plants and broad-leaved weeds. Most grasses are unaffected by high levels of picloram, but certain crops such as beans and tomatoes are extremely susceptible. In addition, although the toxicity of picloram to animals is low, poisoning cases have been reported (Savage and Tessari, 1975). Consequently, reliable methods for the determination of picloram in a variety of matrices are highly desirable.

Most present methods of analysis employ gas–liquid chromatography (GLC) with electron capture or flame ionization detection of picloram derivatives (Moseman and Aue, 1970) and have detection limits in the low parts per billion or picogram range. The virtues of this approach include reasonable selectivity and ability to identify the compound along with excellent detection limits. However the cleanup requirements are exacting, and derivatization procedures are inherently undesirable. Electrochemical techniques, especially pulse polarography, nicely complement the GLC approach. As a rough rule of thumb differential pulse polarography (DPP) gives a relative detection limit five–ten times higher and absolute detection limit about 1000 times higher than GLC. Identification capabilities are also not as good. But the equipment is very inexpensive, reliable, and easy to maintain, and cleanup procedures are frequently not as demanding. An additional difference between GLC and voltammetric techniques deserves comment here. With GLC procedures adequate cleanup is required not only for proper analytical results but also for column and detector maintenance. Inadequate cleanup can therefore result in large amounts of down time and additional labor. In voltammetric techniques, the sample contacts only the electrodes, whose replacement or reconditioning is a trivial process. Therefore the only loss incurred with an inadequately prepared sample is the preparation time itself. Of course in pulse polarography, as in GLC, proper sample cleanup is required to ensure freedom from artifacts introduced by the matrix.

There are many compounds of interest (such as picloram) with insufficient volatility to permit determination by GLC without derivatization but with reducible or oxidizable functional groups which provide the basis for a voltammetric analytical method. We report here on the electrochemical properties of 4-amino-3,5,6-trichloropicolinic acid (picloram) and the related compound 3,6-dichloropicolinic acid (Dowco 290) and use those properties to develop analytical methods for those compounds using the technique of pulse polarography (Osteryoung and Hasebe, 1976). Both fundamental mechanistic studies and the application of these methods to studies of picloram as a herbicide will be the subjects of future papers. Because of the scope and complexity of this work this paper does not include material on sample cleanup and interferences.

EXPERIMENTAL SECTION

Polarographic data were obtained with a PARC Model 174 polarographic analyzer (Princeton Applied Research Corporation, Princeton, NJ) and a PARC Model 174/70 drop timer unless otherwise specified. The polarograms were recorded on an Omnigraphic Model 2000 X-Y recorder (Houston Instrument Company, Austin, TX). The dropping mercury electrode (DME) used had the following characteristics: for picloram concentration studies the mercury flow rate was $m = 1.52$ mg/s and the natural drop time was $t_d = 5.09 \pm 0.02$ s in deionized water at open circuit; for picloram pH studies $m = 1.31$ mg/s and $t_d = 6.6$ s; for Dowco 290 pH and concentration studies $m = 2.02$ mg/s. A platinum wire counter electrode was placed directly in the standard PARC 5–50-mL cell. A presaturated purified nitrogen stream was passed through a Teflon tube into the solution to deoxygenate the solutions. During polarogram measurement the solution was kept oxygen-free by passing nitrogen over the solution surface and the effluent gas was passed through a water trap to prevent air backflow. Measurement of pH was made with a Corning Model 110 expanded scale digital pH meter with standard commercial pH electrodes. Electrodes were standardized daily at two pH values with buffers prepared from Fisher Scientific Buffer Concentrate. All measurements were carried out at room temperature kept constant at 22 ± 2 °C. The chemicals were reagent grade and dissolved in doubly distilled water. Analytical standards were >99.9% (Dow Chemical Corporation) stored at –5 °C and dissolved in methanol. Because of the volatility of the solvent, standards were remade for critical measurements.

RESULTS AND DISCUSSION

Polarographic methods for determination of picloram and Dowco 290 are based on the reduction of these compounds in aqueous solution at the DME. The best polarographic techniques now routinely available are normal pulse polarography (NPP) and differential pulse polarography (DPP). Detection limits in NPP are about ten times higher than in DPP, but NPP is less subject to changes in sensitivity with minor changes in reaction conditions and therefore is favored at higher concentrations. If the limiting current in NPP is diffusion controlled, the sensitivity is especially constant and can be calculated from first principles. Therefore the first objective was to find solution conditions producing well-formed, diffusion-controlled waves.

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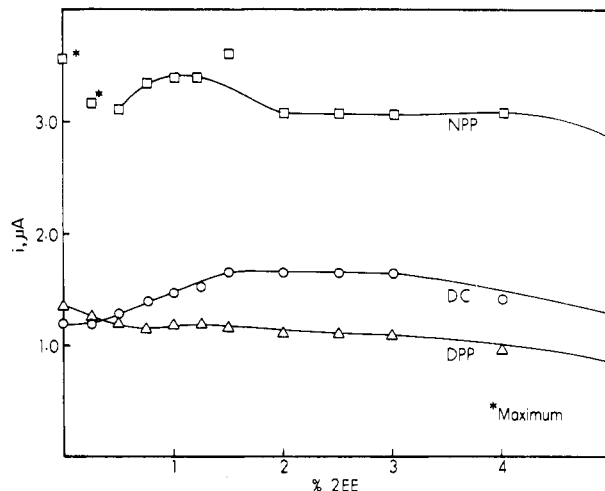
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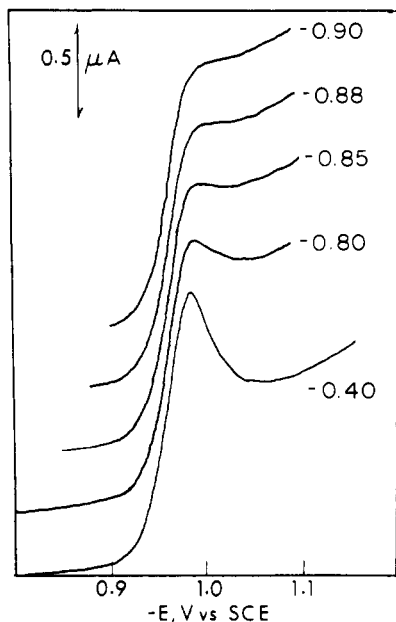
Figure 1. Effect of initial potential on NPP of picloram. Picloram concentration, 5×10^{-6} F; supporting electrolyte, 1.0 F LiCl + 0.02 F H_2SO_4/NaHSO$_4$ (pH 1.9). The number on each curve is the initial potential in V vs. SCE.

Figure 2. Effect of 2EE on the polarographic reduction of picloram. Picloram concentration: 1.0×10^{-4} F; supporting electrolyte: 0.2 F Na_2SO_4, pH 1.8 (H_2SO_4); pulse amplitude (DPP): –25 mV; drop time: 1 s.

A DC polarographic method for picloram has been published (Filimonova and Gorbunova, 1973) as well as a DPP method (Gilbert and Mann, 1973). Filimonova and Gorbunova employed 0.1 M H_2SO_4 or 0.1 M HCl as supporting electrolyte and obtained detection limits of ca. 0.2 mg L^{-1} in aqueous solution and good results for analysis of light sandy soil, heavy soil with high humus content, and dry corn mass. However, these supporting electrolytes are unsatisfactory in the NPP and DPP modes because of the sensitivity of the currents to adsorption effects. Gilbert and Mann used DPP in acetate buffer, pH 4.35, and found a detection limit of 0.02 mg L^{-1}.

We were interested in finding conditions which give well-formed NPP waves. In order to characterize the reduction of picloram by DC polarography in various supporting electrolytes, we measured the head dependence of the limiting current. If $i_l = kh^p$ where i_l is the limiting current and h the head, the exponent p has values 0.56, 0.89, 0.38, and 0.47, respectively, in 2.6×10^{-5} F picloram in H_2SO_4, pH 1; 0.01 F NaOAc/0.3 F HOAc, pH 4.2; 2.0 F Na_2SO_4, pH 1.9; and 2.0 F Na_2SO_4, pH 1.9, 5.6×10^{-2} F Me_2SO. The reduction in H_2SO_4, pH 1, appears to be quasireversible as reported by Filimonova and Gorbunova (they found $p = 0.66$). Gilbert and Mann have suggested that the large value of p in acetate buffer is due to a catalytic reduction mechanism. However, adsorption complications have the same effect and could explain the nonlinear pH dependence and strong effect of ionic strength on the peak current reported by Gilbert and Mann.

At pH 1.9 partial kinetic control is suggested by the low value of p. The NPP waves also showed maxima which were similar to the maxima observed under Filimonova's conditions. The height of the maximum depended on the initial potential as shown in Figure 1. This dependence suggests that the maximum is due to adsorption, because the maximum height depends on the initial potential and the limiting current in the presence of the maximum is less than it is in the absence of the maximum. The dependence of the NPP wave on the initial potential arises from potential dependence of the extent of adsorption of the electroactive material on the electrode. Under the con-

ditions of Figure 1, picloram exists as a neutral molecule (or a zwitterion); its adsorption would be expected to be a maximum at the point of zero charge (pzc) and to decrease at potentials removed from the pzc. According to Figure 1, desorption of picloram begins at about –800 mV vs. SCE and is essentially complete by ca. –900 mV. The decrease in the limiting current when maxima are observed is a complex phenomenon (Flanagan et al., 1977).

In solutions ca. 10^{-2} F in Me_2SO there is no maximum and the value of p approaches the theoretical value of 0.50 for a diffusion-controlled process. Me_2SO was initially used to prepare standard solutions because 10^{-2}–10^{-3} F picloram dissolves readily in this solvent. However, Me_2SO was found to be unsuitable for preparation of standards because 3×10^{-4} F Me_2SO significantly altered the background by decreasing the potential of cathodic breakdown. A concentration of 5×10^{-3} F Me_2SO obscured the picloram peak at high sensitivity.

Ethanol is another good solvent for picloram, but ethanol is sufficiently volatile that it is difficult to control the composition of its mixtures with water. Therefore we investigated an ethanol derivative, 2-ethoxyethanol (2EE), as a cosolvent which would alleviate the adsorption difficulties. The effect of 2EE concentration on picloram reduction is shown in Figure 2. Above 0.5% 2EE the effect of adsorption was not evident in NPP. In the concentration range 2–3% 2EE sensitivities were good and independent of the exact concentration.

Diffusion Control Criteria in Pulse Polarography. Addition of 2EE eliminated adsorption problems in the DC and NPP modes and appeared to give a diffusion-controlled limiting current. However, the dependence of limiting current on the mercury head is a DC test (i.e., it is on the time scale of the drop, a few seconds), while the pulse time scale is in the millisecond range. The necessity of testing for diffusion control on the appropriate time scale is illustrated in Figure 3, which shows the reduction of Dowco 290. The data were obtained using a modified PARC 174 polarographic analyzer (Abel et al., 1976). The NPP polarograms can be compared with the DC polarogram in which the current was measured at the end of a 1-s drop. In DC, the two waves are nearly equal in height and both waves are diffusion controlled according to the criterion of current dependence in drop life. The current is fitted to the equation $i = kt^q$ where i = instantaneous current, t = time in drop life. The q values obtained for

Table I. Diffusion Coefficients for the Picolinic Acids

| compound | conditions | $10^3 n D^{1/2}$ | | |
		DC	NPP	reference
picolinic acid	pH 3.4, McIlvain's Buffer	7.9		Jellinek and Urwin, 1954
picolinic acid	pH 3.4, potassium phthalate	8.8		Tomkins and Schmidt, 1943
picolinic acid	pH 7, B/R buffer	5.9		Volke and Volkova, 1955
picloram	0.1 N H_2SO_4	$(4.5)^a$		Filimonova and Gorbunova, 1973
picolinic acid	pH 4.0, 0.1 F acetate	7.8	7.7	b
6-chloropicolinic acid	pH 1.9, 0.1 F sulfate, 1% 2EE	7.5	5.9	b
Dowco 290, wave 1	0.5 N H_2SO_4, 1% 2EE	8.1	8.3	b
picloram	pH 1.88, 0.1 F sulfate, 1% 2EE	11.0	11.5	b

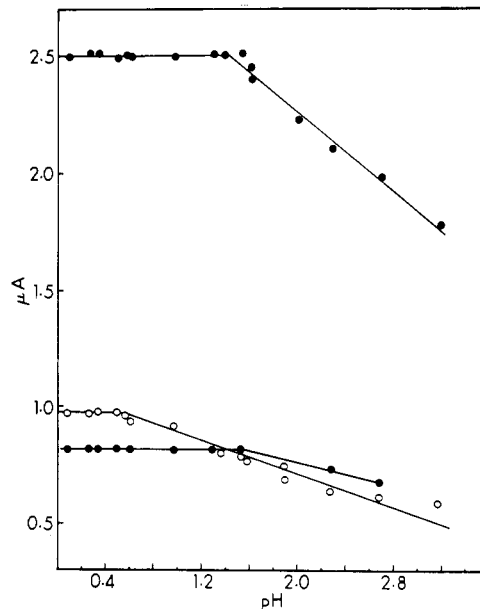[a] A quasi-diffusion controlled wave.   [b] This work.
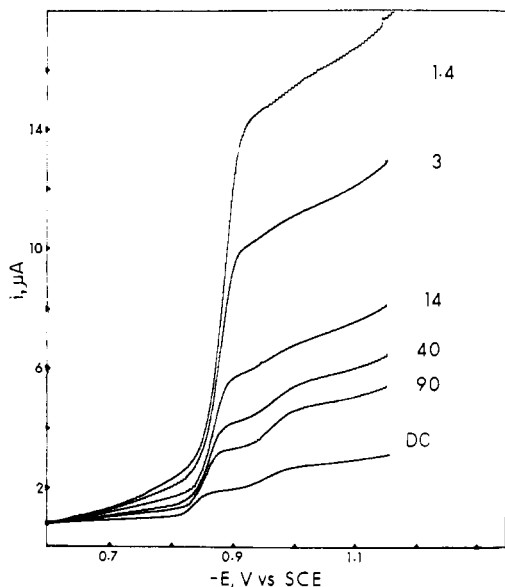
Figure 3. Time dependence of the NPP current for Dowco 290. Dowco 290 concentration, 1.0 × 10⁻⁴ F; supporting electrolyte, 0.2 F Na_2SO_4, pH 1.9 (H_2SO_4) 5% 2EE; sampling time, 0.38 ms; delay time, 900–980 ms; DC measurement time, 90 ms. Numbers on curves are pulse widths in milliseconds.

Figure 4. Effect of pH on limiting current (●) or peak current (○) for wave 1 of Dowco 290. Solid circles: upper curve, NPP; lower curve, DC; open circles: DPP. Dowco 290 concentration, 1 × 10⁻⁴ F; supporting electrolyte, 0.1 F Na_2SO_4 + H_2SO_4, 5% 2EE; pulse amplitude (DPP), -25 mV; drop time, 1 s.

Dowco 290 were as follows: wave 1, 0.23; wave 2, 0.19, which compare favorably with experimental values reported for a system known to be diffusion controlled (Taylor et al., 1949). These values are slightly larger than the q = 0.167 predicted by the Ilkovic equation; this general discrepancy has been explained (Lingane, 1953).

As the pulse width in NPP is shortened, the second wave height diminishes with respect to the first; at pulse widths of 2 ms or less no second wave appears. Thus an electrochemical process can be diffusion controlled on a DC time scale, but occur too slowly to be seen on a pulse time scale. Figure 3 also illustrates the enhancement of signal obtained with short-pulse widths as predicted by the Cottrell equation (Abel et al., 1976).

To test for diffusion control in NPP, the current-time behavior is examined during pulse lifetime. In this case $i = k't^r$ where t is the time after pulse application. The theoretical value for diffusion control is r = 0.50, as predicted by the Cottrell equation. In 0.1 F Na_2SO_4, pH 1.9 (H_2SO_4), 1% 2EE, 10⁻³ F and 10⁻⁴ F picloram gave values of r of -0.503 and -0.496, respectively. For Dowco 290, pH 1.88, 5% 2EE, r values were 0.39 and 0.29, respectively, for the first and second waves. However in 0.5 F H_2SO_4, 5% 2EE, the first wave had r = 0.492 while the second had r = 0.422. Thus under these conditions the first wave is diffusion controlled and the second almost diffusion controlled.

The diffusion coefficients measured under diffusion-controlled conditions and expressed as $nD^{1/2}$ are compared to literature values for the model compound picolinic acid in Table I. The value we obtained for picolinic acid is within the range of these literature values. There is no unanimity in the literature on the number of electrons or the electrode reduction process for picolinic acid; however, the preponderance of the evidence suggests pyridine carboxylic acids in moderate pH ranges are reduced to the hydrated aldehyde in a 2e⁻ diffusion-controlled wave (Knobloch, 1952; Nagata and Tachi, 1954; Lund, 1963; Tissier and Aquotin, 1973). The earlier assertion of Jellinek and Urwin and of Tompkins and Schmidt that the picolinic acid wave is due to catalytic hydrogen evolution from the pyridyl nitrogen is not supported by all of the evidence presented in their papers (Jellinek and Urwin, 1954; Tompkins and Schmidt, 1943). Lund's isolation of the corresponding aldehydes from controlled potential electrolyses at pH 2.3 of isonicotinic and picolinic acids is evidence for the 2e⁻ reduction (Lund, 1963). Recently, the controlled potential electrolysis of picolinic acid to the picolinic aldehyde at pH 2 was reported (Brown et al., 1975). The same paper reports a 4e⁻ reduction to 2-hydroxymethylpyridine in 46% chemical yield in bulk electrolysis at pH 4.8. Polarographic studies report pH-independent limiting currents in the pH range 1–8, which suggests that only the 2e⁻ reduction occurs under polarographic conditions (Jellinek and Urwin, 1954; Tompkins and Schmidt, 1943).

From the agreement of diffusion coefficients in Table
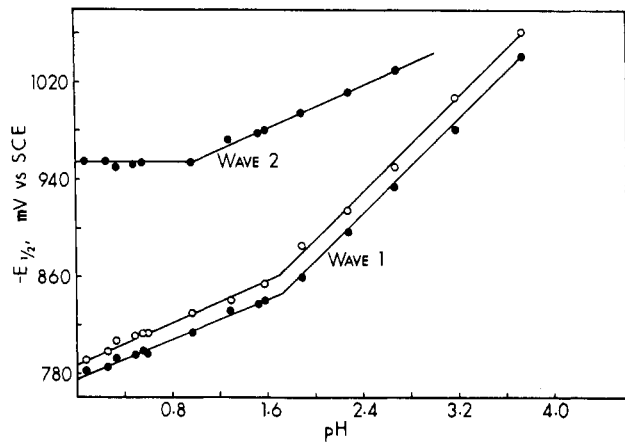
Figure 5. Effect of pH on half-wave [DC (●)] or peak [DPP (○)] potentials for reduction of Dowco 290. Conditions as in Figure 4.
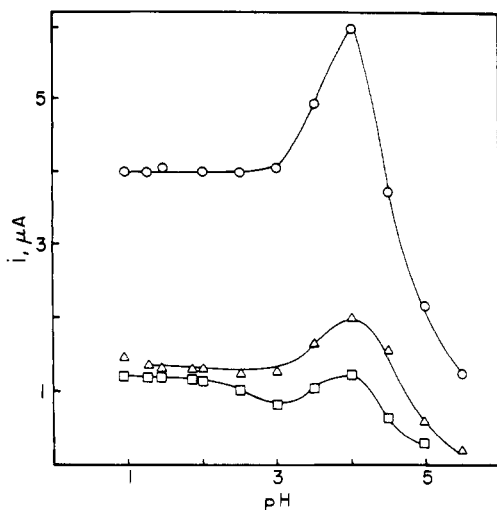

Figure 6. Effect of pH on the limiting current [DC (△), NPP (○)] or peak current [DPP (□)] for reduction of picloram. Picloram concentration, 1×10^{-4} F; supporting electrolyte, 0.1 F Na_2SO_4 or 0.1 F NaOAc + HOAc, 1% 2EE; pulse amplitude (DPP); -25 mV; drop time, 1 s.
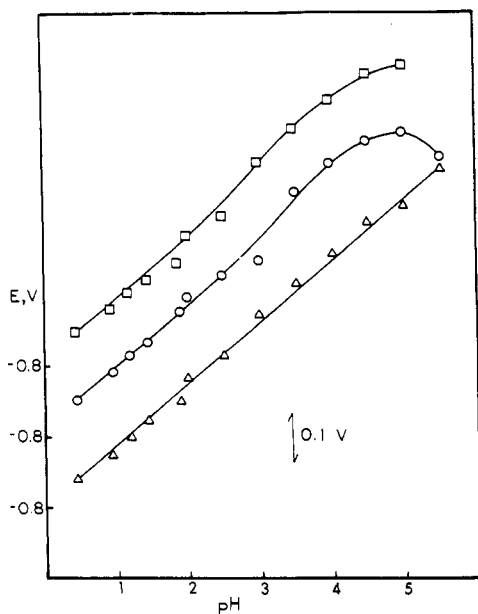
Figure 7. Effect of pH on the half-wave [DC (△), NPP (○)] or peak [DPP (□)] potentials for reduction of picloram. Conditions as in Figure 6.
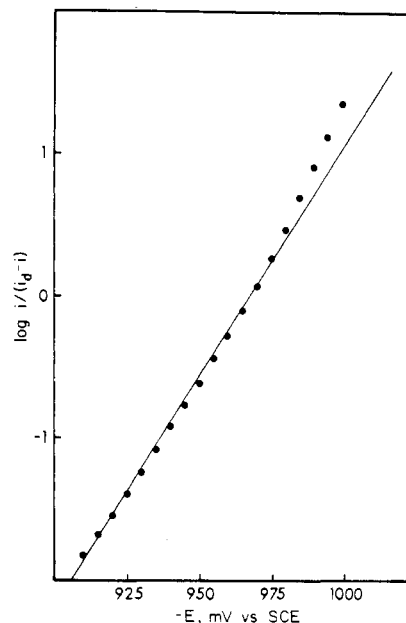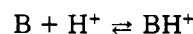

Figure 8. Logarithmic analysis of the NPP wave for picloram reduction. Initial potential: -750 mV vs. SCE. Other conditions same as Figure 6.
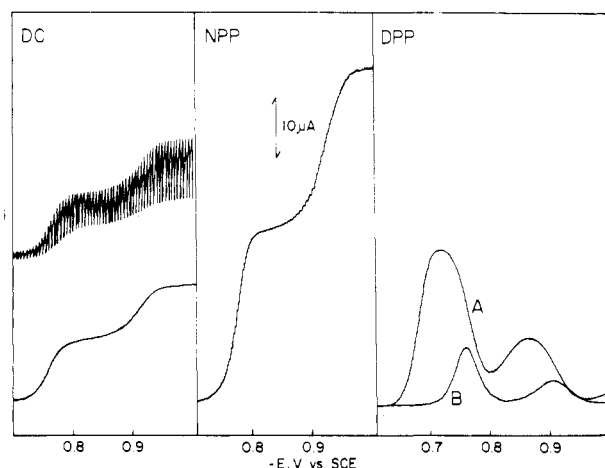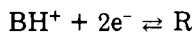

Figure 9. Polarograms of Dowco 290. Dowco 290 concentration, 1×10^{-4} F; supporting electrolyte, 0.5 F H_2SO_4, 5% 2EE; sweep rate, 1 mV/s; pulse amplitude (DPP), (A) -100 mV, (B) -25 mV; drop time, 1 s.

I, it is reasonable to assume that 6-chloropicolinic acid is reduced in a 2e⁻ process. The -24% difference between the NPP and DC estimates of $nD^{1/2}$ for 6-chloropicolinic acid suggests the current is not diffusion controlled in NPP. Dowco 290 is reduced in two 2e⁻ waves; the more cathodic wave is only quasi-diffusion controlled. The larger value of $nD^{1/2}$ for picloram might be explained by assuming $n = 3$. Although this would give a diffusion coefficient close to the diffusion coefficients for Dowco 290, 6-chloropicolinic acid and picolinic acid, this explanation would require catalytic hydrogen reduction or dimerization either of which is unlikely given the linear current–concentration response from 10^{-7} to 10^{-3} F. Thus we conclude picloram simply has a larger value of D and $n = 2$.

Effects of pH. The effects of pH on the reduction of Dowco 290 and picloram are shown in Figures 4–7. The data are in agreement with a mechanism requiring prior protonation of the neutral molecule. In this scheme

$$B + H^+ \rightleftarrows BH^+$$

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$$BH^+ + 2e^- \rightleftarrows R$$

which is typical of organic reductions in protic solvents, B represents the neutral molecule and R the primary reduction product. The 2EE concentration was increased to 5% in these experiments to eliminate the adsorption maximum on the NPP wave at pH 1.1. A classical maximum of the first kind was observed on wave 2 in the DC mode at pH 1.3 and was also eliminated at the higher 2EE concentrations. Dowco 290 shows (Figures 4 and 5) a break in the slope of the half-wave potential shift with changing pH for wave 1 at pH 1.8, which coincides with a decrease in the limiting current in the DC and NPP modes. A preprotonation reaction which becomes current limiting at high pH would account for this behavior. The DPP peak current decreases beginning at a lower pH, 0.6. The difference between the NPP and DPP pH dependence illustrates the analytical importance of being aware that the DPP current is more sensitive than the NPP current to changes in reaction conditions. On the basis of Figure 5, 0.5 N H_2SO_4 was chosen as the supporting electrolyte for the analysis of Dowco 290 to ensure that the currents would be insensitive to minor pH variation.

For the analysis of picloram, the medium of choice is 0.05 F $NaHSO_4$/0.05 F H_2SO_4 buffer and 2% 2EE in the range 1 < pH < 2 for all modes (Figures 2, 6, and 7). About a 50% increase in current is observed in the pH region 3–4. Similarly, a 75% increase in current was observed using 1.0 F LiCl supporting electrolyte and B/R buffer (no 2EE); the maximum value occurred at pH 3.5. The reason for this current increase was not extensively investigated. However, adsorption phenomena are suggested by the i-t behavior reported above. Corresponding changes in the $E_{1/2}$/pH curves at pH 3.0 also suggest complications in the reduction. Therefore, although the sensitivity can be increased by working in other media, this advantage is more than offset by the disadvantage of uncertainty about the constancy of sensitivity.

Effect of Modulation Amplitude. The analyst can change the modulation amplitude, the magnitude of the potential pulse applied in DPP, with the usual trade-off between sensitivity and resolution. In general, increasing the amplitude gives more current and hence greater sensitivity. Smaller pulse amplitudes give better resolution and less instrumental error (Christie, et al., 1973).

The reductions of both picloram and Dowco 290 are irreversible as shown by cyclic voltammetry at scan rates up to 400 mV s^{-1} and reverse pulse polarography (Kirowa-Eisner and Osteryoung, 1979). For picloram at 5 × 10^{-5} F in 0.1 F Na_2SO_4, pH 1 (H_2SO_4), 1% 2EE peak width, peak heights, and peak potentials have the expected theoretical values for a reversible 2e⁻ reduction over the range of pulse amplitude 5–100 mV (scan rate, 1 mV s^{-1}; drop time, 1 s). The same results are obtained for the first wave of Dowco 290, 1 × 10^{-4} F, in 0.5 F H_2SO_4 5% 2EE with the exception that the peak widths are about 7 mV more narrow than predicted. The latter is a common effect of adsorption.

The plot of E vs. the appropriate log function of the current (Figure 8) is linear through the half-wave potential with slope 32 mV per decade which can be compared with the theoretical slope for a reversible wave of $59/n$ mV per decade (n = 2). Polarographic waves which are known to be irreversible by other criteria, but display the wave shape of a reversible wave are well known (Perrin, 1969). Since NPP polarograms for picloram and Dowco 290 have the shape of a reversible wave up to the half-wave potential, the DPP peak currents, and to a lesser extent the peak widths, obey the equations for reversible waves, for the
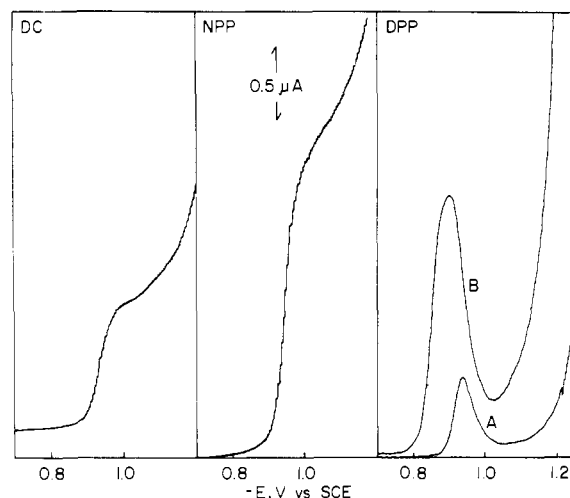
Figure 10. Polarograms of picloram. Picloram concentration, 1 × 10^{-4} F; supporting electrolyte, 0.1 F $NaHSO_4$, pH 1.9 (H_2SO_4), 1% 2EE. Other conditions same as Figure 9.

peak currents depend almost entirely on behavior of the wave on its rising portion ($E < E_{1/2} + \Delta E/2$). This pseudo-reversible behavior arises under certain kinetic conditions when the product of the electron-transfer reaction is involved in a subsequent chemical reaction (Kivalo, 1955). The reduction of the chloropicolinic acids in a rapid electron transfer followed by a slower, irreversible chemical reaction would account for the behavior on the first half of the wave. The simple theory predicts a linear relation between E and the log of the current function. Thus a more complex pathway is suggested by the change in slope observed for the wave past the half-wave potential.

The dependence of peak height and width on pulse amplitude suggest an optimum pulse amplitude for routine analysis. The peak current increases nearly linearly with pulse amplitude up to −50 mV but doubling the pulse amplitude to −100 mV produces only about 25% increase in the current. Changing the pulse amplitude from −5 to −50 mV has little effect on the peak width while the change from −50 to −100 mV almost doubles the peak width. Thus a −50 mV pulse amplitude gives good sensitivity without degrading the resolution.

Concentration Dependence and Detection Limit. The reduction waves for 1.0 mM of the chloropicolinic acids using the solution conditions of choice are shown in Figures 9 and 10. The threefold increase in sensitivity between DC and NPP is that predicted by theory.

The two waves for Dowco 290 give rise to two peaks in DPP. The irreversibility of the second wave causes the second peak to have a smaller amplitude than the first, and therefore only the first wave is used for analysis. The second peak is useful for identifying Dowco 290 at higher concentrations. At lower concentrations, the second peak is obscured by the cathodic breakdown current. Because of the resolution problem, one can observe a peak at 2 × 10^{-7} F using a pulse amplitude of −25 mV while the peak is not discernible below 1 × 10^{-6} F using a pulse amplitude of −100 mV.

The current–concentration curves for picloram and wave 1 of Dowco 290 are shown in Figures 11 and 12. A deviation from linearity is present above 1 × 10^{-4} F picloram in DPP and 5 × 10^{-4} F in NPP. The solubility of picloram at pH 2.0 has been reported to be 5.7 × 10^{-4} F at 20 °C at an unspecified ionic strength (Cheung and Biggar, 1974). We have verified this measurement and demonstrated that in this concentration range the curvature in the calibration
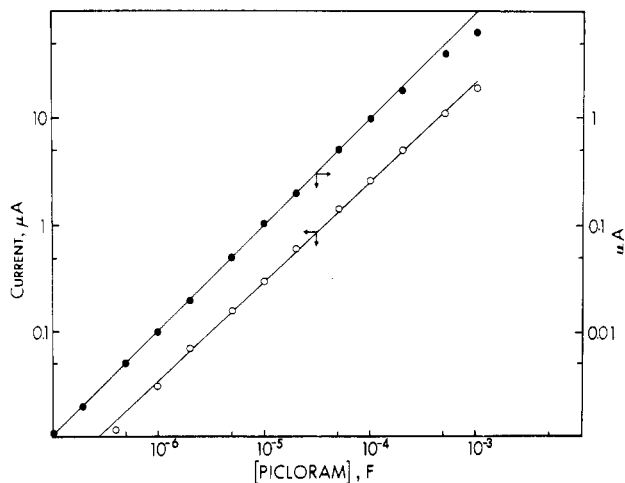
Figure 11. Calibration curve for picloram by DPP (●) and NPP (○). Pulse amplitude: −25 mV. Other conditions same as Figure 10.
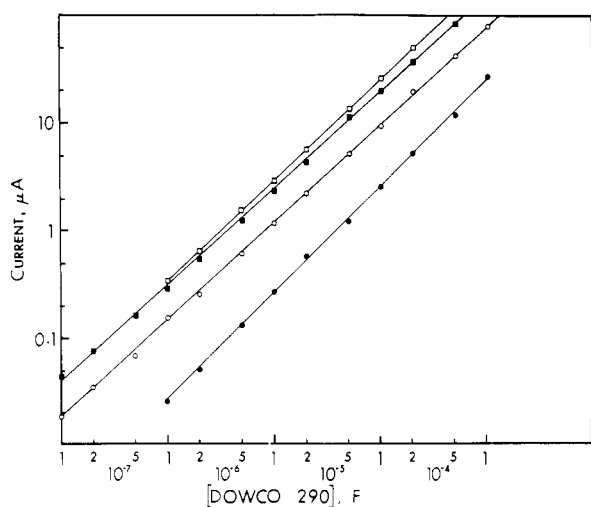
Figure 12. Calibration curve for Dowco 290 (wave 1). NPP (●); DPP, pulse amplitude: −25 mV (○), −50 mV (■), −100 mV (□). Other conditions same as Figure 9.

curve is due to slow attainment of solubility equilibrium when aliquots of standard solution are added to the test solution. In equilibrated solutions the limiting current shows no increase with added amounts of picloram above the solubility limit (Osteryoung and Whittaker, 1979).

Detection limits for picloram and Dowco 290 were calculated according to the formula $dl = ts/m$ where dl is the detection limit, t is the one-sided t statistic at the 95% confidence level, s is the pooled standard deviation of an individual value from the calibration curve, and m its slope.

Since s is an absolute value, estimates were made only for dilute solutions: 1–500 × 10^{-7} F for picloram and 0.5–100 × 10^{-7} F for Dowco 290. For Dowco 290 in 0.5 F H_2SO_4, 5% 2EE the sensitivities are 11.6 and 25.0 μA $(mM)^{-1}$ and detection limit 1 × 10^{-7} M (17 μg L^{-1}) at pulse amplitudes of −25 and −50 mV, respectively, while the corresponding values for picloram, 0.1 F Na_2SO_4, pH 1.9, 1% 2EE, pulse amplitude −25 mV, are 10.3 μA $(mM)^{-1}$ and 6 × 10^{-8} M (14 μg L^{-1}). Thus the basis exists for the development of detailed methods for the determination of picloram and Dowco 290 in formulations and other sample types of interest.

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