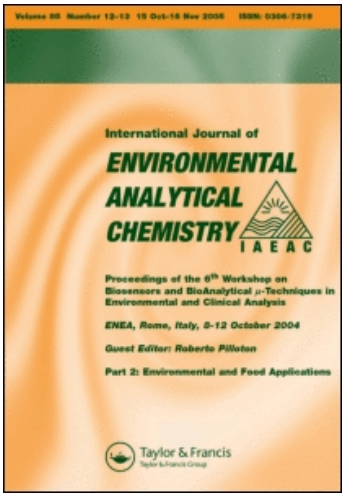


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# Herbicide Analysis by Pulse Polarography-Picloram†

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The herbicide picloram, 4-amino-3,5,6-trichloro-picolinic acid, can be determined at 0.02 ppm, without concentration, by pulse polarography. The effects of pH, ionic strength, and buffer constituents on the catalytic hydrogen process have been studied to optimize conditions for highest sensitivity for picloram. A buffer solution 0.01M sodium acetate—0.026M acetic acid was used to evaluate the analysis of a natural water system. Errors range from 3–8% (relative) in the 0.05–0.20 ppm picloram range with precisions of ±5% (relative) or better. Interferences with 0.1 ppm picloram from 100 ppm Cr(VI) and Zn(II) are severe; neither ion interferes at 1 ppm. Fe(III) interference can be eliminated by masking with EDTA. Mn(II), Cu(II), and Pb(II) do not interfere at 10 ppm.

## INTRODUCTION

The analysis of picloram (4-amino-3,5,6-trichloro-picolinic acid) in water and soil is usually carried out by gas chromatography with an electron capture or an ionization detector. The method is very sensitive, with detection limits of a few tenths of a ppb in water to 20 ppb in soil.[1–4] The method usually requires a time-consuming clean-up procedure followed by esterification of the acid. Bioassay methods for the determination of picloram are well known but are also rather time-consuming.[5–7] Cheng[8] notes that extreme sensitivity is not always required for a particular sample and reported a colorimetric

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procedure for picloram in soil which avoids lengthy sample preparation prior to the analysis. The detection limit was reported as 0.5 ppm of picloram in an aqueous extract and 1–25 ppm picloram were determined in soils. The colorimetric analysis must be done under a photographic safety light, due to the photochemical decomposition of the colorimetric reaction product. The U.S. Food and Drug Administration has released registry requirements for picloram which range from 0.05 ppm in milk to 80 ppm in or on forage grasses.[9] There is a need for simple, rapid methods for the determination of picloram which need not have the extreme sensitivity of the more time-consuming gas chromatographic or bioassay methods.

Many biocides can be determined polarographically.[10–12] Picloram has been detected at 0.08 ppm by single-sweep (oscillo or cathode-ray) polarographic methods.[13] The present work describes a study undertaken to optimize the analysis of picloram by pulse polarography to yield reproducible, rapid, and relatively sensitive determinations. The results describe a method for picloram in water which is 4–5 times more sensitive than other reported polarographic methods and is more rapid than the conventional bioassay or gas chromatographic techniques. In addition, the pulse method is about 10 times more sensitive than the colorimetric analysis and can be conducted in a normally lighted laboratory. As little as 0.02 ppm picloram can be detected by pulse polarography.



## EXPERIMENTAL

### Apparatus

A Melabs Pulse Polarographic Analyzer Model CPA–3 was used in the derivative mode with constant-amplitude pulses. The instrument[14] and rationale of pulse polarography[15] have been published elsewhere. Polarograms were recorded with a Hewlett–Packard Mosely Model 135 AM x-y recorder. A 57-cm mercury head was maintained and all potential measurements were made with a saturated calomel electrode (SCE) reference. The capillary used had characteristics of $m = 0.806$ mg/sec and $t = 5.13$ sec in 0.01M sodium acetate—0.026M acetic acid (open circuit). Membrane filter apparatus (Millipore Corp.) was used to filter turbid samples.

### Materials

All supporting electrolytes and other reagents were analytical-grade materials. Purification of these materials was found to be unnecessary although they do contain electroactive impurities. There is no interference of these impurities, however, with the picloram peak. Storage of solutions in polypropylene or polyethylene bottles was found to be advisable to avoid peaks due to other electroactive species found upon storage in glass vessels. Picloram (99.9%) was supplied through the courtesy of the Agricultural

Research Service, Flagstaff, Arizona. Stock solutions of picloram (20–50 ppm) showed no diminution in concentration over a 3-month period. Longer storage periods were not used in this work.

### Procedure

Stock solutions of picloram (50 ppm) were prepared by dissolving 25.0 mg of the acid in 500 ml of water to which 0.2 ml of 50% NaOH had been added. After the picloram had dissolved, hydrochloric acid was added to bring the pH to 7. Aliquots of the stock solution were taken, buffer constituents added and the solutions diluted to known volumes. A convenient procedure in the case of an acetic acid (HOAc)-sodium acetate (NaOAc) buffer was to add solid sodium acetate to yield a solution of the desired concentration and then to add glacial acetic acid until the pH of the solution was the desired value. In the case of water samples, an aliquot was taken, buffer constituents were added and the solution was diluted to a known volume. Turbid water samples were passed through a 5.0 micron poresize membrane filter prior to preparation for polarography.

A 10-ml aliquot of the buffered solution was placed in the polarographic cell and deoxygenated with oxygen-free nitrogen for 5 min prior to obtaining the polarogram between $-1.2$ and $-1.5$ V with a voltage sweep rate of 0.1 V/min and $-30$ mV pulses.



## RESULTS AND DISCUSSION

The behavior of picloram was studied with respect to pH, buffer constituents, ionic strength, and temperature. The results are summarized in the accompanying Figures and Tables. Figure 1 shows a typical polarogram of 0.25 ppm picloram in 0.01M sodium acetate-0.026M acetic acid (pH 4.35). The lower polarogram is the buffer-electrolyte solution only. The peak potential is $-1.28$ V and the peak height above the buffer-elecrolyte is a measure of the current resulting from the electrochemical process. A straight-line calibration curve, peak height versus picloram concentration, is obtained between 0.02–2.4 ppm picloram. Higher picloram concentrations were not used in this work.

Picloram gives rise to a catalytic hydrogen electrochemical process. The process is well known in the polarography of nitrogeneous bases.[16–18] If picloram is considered a base, B, the following mechanism has been suggested as the reaction it undergoes at the mercury electrode.[18]

$$B + DH^+ \rightleftarrows BH^+ + D \qquad (1)$$

$$BH^+ + e^- \rightleftarrows BH \qquad (2)$$

$$2BH \rightleftarrows 2B + H_2 \qquad (3)$$

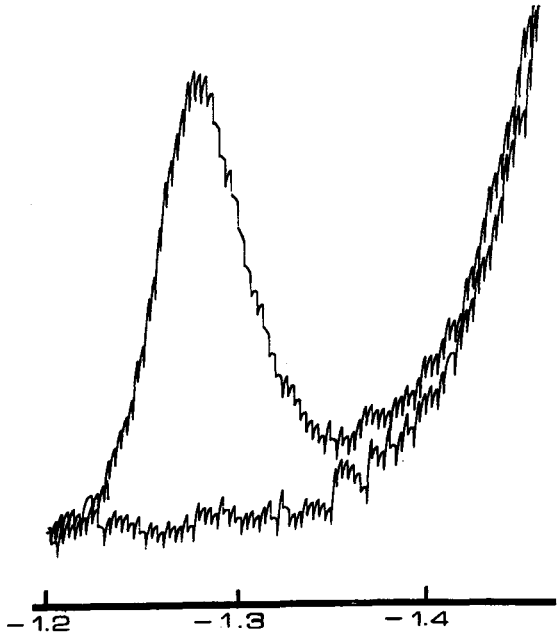


FIGURE 1 Pulse polarogram of Picloram. Upper curve: 0.25 ppm Picloram. Lower curve: 0.01M sodium acetate—0.026M acetic acid only. Pulse amplitude: −30 mV.

Picloram is protonated (reaction 1) and diffuses to the mercury electrode where it and the basic form, B, are adsorbed. The adsorption process of the acid form is particularly dependent on the electrode potential. The adsorbed, protonated species accepts an electron, and a radical, BH, is formed (reaction 2). A second-order decomposition (reaction 3) takes place with the evolution of hydrogen and the regeneration of the original picloram base. The original picloram can enter the reaction sequence again, with the net result that it acts as a catalyst in the evolution of hydrogen.

The current which results from this process is dependent upon many experimental parameters, including the equilibrium constant of reaction 1 as well as the rates of all three reactions.

*Effect of pH (Figure 2) and buffer capacity* The initial acidity of the solution in the vicinity of the electrode will influence the ratio of the concentrations of the acid and base forms of picloram, $[BH^+]/[B]$, and the rate of the protonation of B. As the reaction sequence continues the acidity at the electrode surface will decrease significantly unless the entire solution is well buffered. As the pH of the solution increases, the ratio $[BH^+]/[B]$ and rate of protona-

tion of B decrease. Since $BH^+$ is the electrochemically active species, the current can be expected to decrease at high pHs. At low pHs the current also decreases. It has been suggested that the basic form of nitrogenous compounds is more highly adsorbed on the electrode surface than the acid form. Therefore, as the pH decreases less basic form is available to the surface and if adsorption is an important feature of the reaction mechanism, the current would decrease.

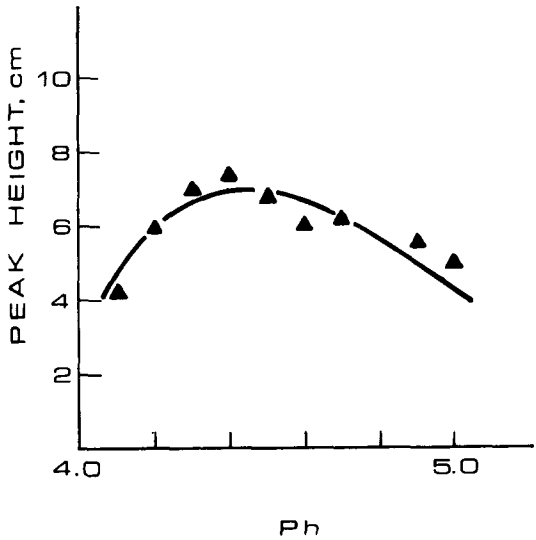


FIGURE 2 Picloram peak height as a function of pH. Picloram 0.08 ppm. Sodium acetate—acetic acid buffer. Ionic strength constant 0.020. Pulse amplitude −30 mV.

The pH in the vicinity of the electrode surface tends to increase with the consumption of protons in the reaction mechanism. Solutions of higher buffer capacity tend to give larger peak heights since the pH at the electrode surface is more nearly constant than in a solution with lower buffer capacity.[17] However, solutions with very high buffer capacity also have higher ionic strengths which lowers the peak height (Figure 3). The solution of 0.01M sodium acetate–0.026M acetic acid, at a buffer capacity of 0.019, was used throughout this work.

*Effect of ionic strength* (*Figure* 3) Mairanovskii has shown that catalytic hydrogen processes which have a high degree of surface character, i.e., in which substantial adsorption at the electrode surface takes place, are dependent upon the electrical double layer at the electrode. An increase in ionic strength generally alters the electrical double layer in such a way as to decrease the current,[18] as observed in this work.

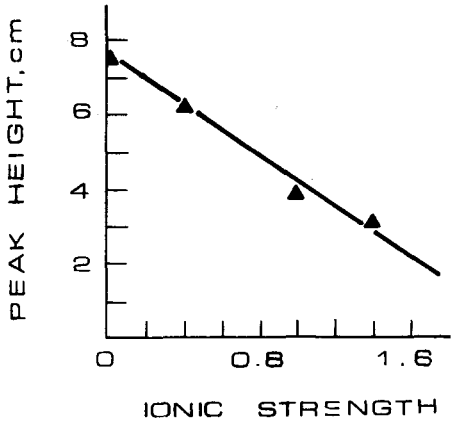


FIGURE 3 Picloram peak height as a function of ionic strength. Picloram 0.08 ppm. Sodium chloride used to adjust the ionic strength of a sodium acetate—acetic acid buffer, pH constant at 4.35. Pulse amplitude −30 mV.



*Effect of buffer constitutnets (Table I)* The nature of ionic buffer constituents can sometimes alter the electrical double layer characteristics and, therefore, the peak current height.[18] This was not observed with the constituents used in this work. The acetate-acetic acid system was chosen for most work as this buffer solution yielded more reproducible and less 'noisy' polarograms than the phosphate or citrate solutions.

TABLE I

Effect of buffer (pH 4.35) constituents on sensitivity

| Constituents | Sensitivity CM/ppb |
|---|---|
| Disodium phosphate-citric acid | 0.15 |
| Trisodium tartrate-tartaric acid | 0.13 |
| Sodium acetate-acetic acid | 0.14 |

*Effect of mercury head* The catalytic hydrogen peak height is proportional to the mercury head, i.e., $p = kh^x$. If $h$ is the height of the mercury above the solution in cm and p the picloram peak height in cm, then $k = 0.36$ and $x = 0.70$. This effect has an important analytical significance in that as the head is raised higher, a greater sensitivity for picloram is obtained.

*Effect of temperature* The picloram height increases by 1.3% per degree rise in temperature between 25–38°C. This agrees with Mairanovskii's report with similar compounds and is interpreted to indicate that an increase in the rate constant of catalyst protonation is compensated for by a decrease in the catalyst adsorption on the electrode surface.[19]

*Interferences* Solutions of picloram have been exposed to a normally illuminated laboratory for over four weeks with no deleterious effects. There was no diminution of peak height from a standard picloram solution exposed to bright sunlight for 8 hr. Picolinic acid yields a current peak at −1.19 V compared to −1.28 V for picloram. A ten-fold excess of picolinic acid causes an interference with picloram leading to a negative error of 5–10% (relative).

Diverse electroactive ions were tested at 100-fold excesses over picloram (10 ppm metal ion, 0.1 ppm picloram) in both the acetate and the phosphate-citrate buffer system. Mn(II), Cu(II), and Pb(II) yield no interfering peaks. Fe(III), Cr(VI), and Zn(II) yield peaks which severely overlap the picloram peak. The Fe(III) interference is eliminated by adding 100 mcl of a saturated solution of disodium (ethylenedinitrilo) tetraacetate to 10 ml of the solution in the polarographic cell. Cr(VI) and Zn(II) must be separated prior to the analysis if they are in a 100-fold excess over picloram. At a 10-fold excess, 1.0 ppm metal–0.1 ppm picloram, neither Cr(VI) nor Zn(II) yield an interference as their peaks, relative to the picloram peak, are not detectable.

*Analysis of natural water samples (Table II)* Picloram was added to an untreated natural water sample, passed through a 5.0-micron poresize membrane filter to remove particulate matter, buffered at pH 4.35, and analyzed. The quantity of picloram in the sample was determined with a previously prepared working curve and by a standard addition method. The unspiked water contained no detectable picloram. Errors ranged from 3.2–8.1% (relative) in the 0.05–0.20 ppm concentration range. Either a

TABLE II

Analysis of picloram in natural water

| Picloram added (ppm) | Picloram found (ppm) | Error (%) |
|---|---|---|
| 0.050 | 0.048[a] | 3.2 |
| 0.050 | 0.054 | 8.1 |
| 0.12 | 0.13 | 3.7 |
| 0.20 | 0.20 | 0.0 |

[a] Determined by standard addition; all other values from a working curve.

working curve or standard addition method can give analyses to within 10% (relative) accuracy. Table II gives results of single analysis only at each concentration but the precision is typically ±5% (relative) on duplicate analyses.

## CONCLUSIONS

Pulse polarography can be applied to the analysis of picloram in water with rapidity and yield reproducible results with a limit of direct detection of 0.02 ppm. Possible interference from metal ions must be taken into consideration. The analysis can be expected to be able to be applied to a variety of other herbicides, including paraquat, diquat, morfamquat, and barban.[13] It would be particularly important, however, to optimize the pH of the solution to yield maximum sensitivity for the individual herbicide as this variable is largely a function of the $pK_a$ values for each herbicide.



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