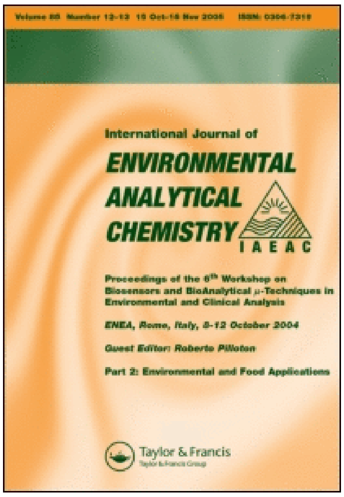

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ADSORPTIVE STRIPPING DETERMINATION OF TRIFLURALIN ON A GLASSY CARBON ELECTRODE

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The herbicide trifluralin was analysed by adsorptive stripping voltammetry on a glassy carbon electrode. The linear concentration range was 2.5×10^{-7} M – 1.25×10^{-6}M when using 5-min preconcentration at open circuit conditions in Britton-Robinson buffer of pH 7.0. The detection limit of trifluralin was 2.5×10^{-8}M. The relative standard deviation was 3.3 % at a concentration of 1.0×10^{-6}M (n=5). The method was applied to the determination of trifluralin in soil with good recovery.

Keywords: Trifluralin; cyclic voltammetry; adsorptive voltammetry

INTRODUCTION

Electrochemical techniques have been widely used for the determination of nitropesticides.[1–5] Southwick *et al*[3] have studied the polarographic behavior of several dinitroaniline herbicides and attempted to correlate their mechanism of reduction to their relative toxicity in the environment. Differential pulse voltammetry and adsorptive stripping voltammetry have been used to determine a number of nitrophenols, used as constituents of the commercial plant growth stimulator, Sviton.[4] The polarographic behavior of a series of nitropesticides, including trifluralin, was studied recently by Kotoušek and Opravilová.[5]

Voltammetry on glassy carbon electrode is generally employed for oxidative measurements.[6] Applications of this electrode to the determination of reducible species are limited owing to their small potential range on the reduction side. However, it has been successfully used for the electroreduction of nitrocom-

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pounds owing to the ease of reduction of nitro group within the cathodic potential range.[7,8]

The aim of the present study was to develop a method for the determination of trifluralin by adsorptive stripping voltammetry on a glassy carbon electrode and to apply it to artificially contaminated soil.

EXPERIMENTAL

Reagents

A stock solution (1×10^{-3} M) of trifluralin (Elanco) was prepared in pure ethanol and stored at 4°C in the dark. Appropriate standard solutions were then prepared daily by subsequent dilution with ethanol. Britton-Robinson buffers (0.04 M in each of acetic, o-phosphoric, and boric acids; adjusted to the required pH with 0.2 M sodium hydroxide solution) were used as supporting electrolytes. All the chemicals used were of AnalaR-reagent grade and all solutions were prepared with doubly distilled water.

Apparatus

Cyclic voltammetry measurements were performed with an Oxford PVSU potentiostat connected to a Philips PM 8043 X-Y recorder. Differential pulse polarography measurements were made with a SARGENT-WELCH model 4001 voltammetric analyzer (USA). A three-electrode system was used; the working electrode was glassy carbon electrode with an apparent surface area of 28 mm^2 (G0021); the reference electrode was Ag/AgCl/(3M KCl) separated by a salt bridge and all potentials reported here are referred to this electrode; a Pt wire was the counter electrode.

A SCHOTT GerÄte digital pH-meter (Germany) with glass combination electrode was used for pH measurements, performed at room temperature.

Procedure

The GCE was polished, at the start of the work, with an aqueous slurry of 0.5 μm alumina powder (K0015) on a damp silk cloth until a mirror-like finish was obtained. After each measurement the electrode surface was renewed by wiping the electrode surface with a soft tissue wetted with acetone and thoroughly rinsed with water. The supporting electrolyte solution (20 ml) with aliquot of trifluralin was added to the cell and degassed by purging with purified nitrogen for 10 min. A flow of nitrogen was maintained over the solution during measurement. The accumulation of trifluralin at the working electrode was carried for a selected time while the solution was stirred at 400 rpm. The stirring was then stopped, and after 15-rest period, a linear sweep or a differential-pulse voltammogram initiated in the negative direction were recorded.

RESULTS AND DISCUSSION

Preliminary voltammetric investigation of trifluralin on a glassy carbon electrode in solutions of different pH values in presence of high contents of organic solvent in the voltammetric cell showed no adsorptive accumulation of trifluralin at the electrode due to its surface coverage by solvent molecules. Thus, the compound was studied at concentration below 1 mg /L in aqueous buffered media.

Figure 1 shows a typical cyclic voltammogram of 1×10^{-6} M trifluralin in a solution of pH 4.0. Trifluralin shows unresolved pair of peaks R_1, R_2 at – 0.58 and – 0.70 V. When the scan was reversed, two oxidation peaks O'_1, O'_2 appeared, to which two corresponding reduction peaks, R'_1, R'_2 were apparent after the second sweep. A third step appeared at more negative potential and became more pronounced as the accumulation time increased. The third peak may be due to a time-dependent process; probably the hydrolysis of trifluralin into secondary amine and phenolate derivative by nucleophilic attack of water. Such attack may be facilitated by the mesomeric-electron withdrawal effect of both nitro groups in addition to the inductive effect of the trifluoromethyl group.[9] The reduction of nitro groups in phenolate derivative occurs at more negative potentials compared to the parent compound.[5] The unresolved pair of peaks R_1, R_2 corresponds to the simultaneous reduction of both nitro groups to the corresponding hydroxylamines.[1] The hydroxylamine is no longer reduced to the amine derivative as a result of the strongly reduced electron density at the hyroxylamino group due to the presence of electrophilic trifluoromethyl group. The reversible redox steps R'_1, O'_1 and R'_2, O'_2 may correspond to the formation of the nitroso-hydroxylamine couples of the parent compound and the phenolate derivative.

Figure 1 also compares the cyclic voltammograms recorded before (A) and after (B) 2-min preconcentration at open circuit potential from a solution stirred at 400 rpm. The peak was much enhanced after preconcentration indicating that the trifluralin was strongly adsorbed on the electrode surface. The height of the trifluralin reduction peak was much reduced when the cyclic scan was repeated on the same surface indicating the adsorption of the reduction product on the

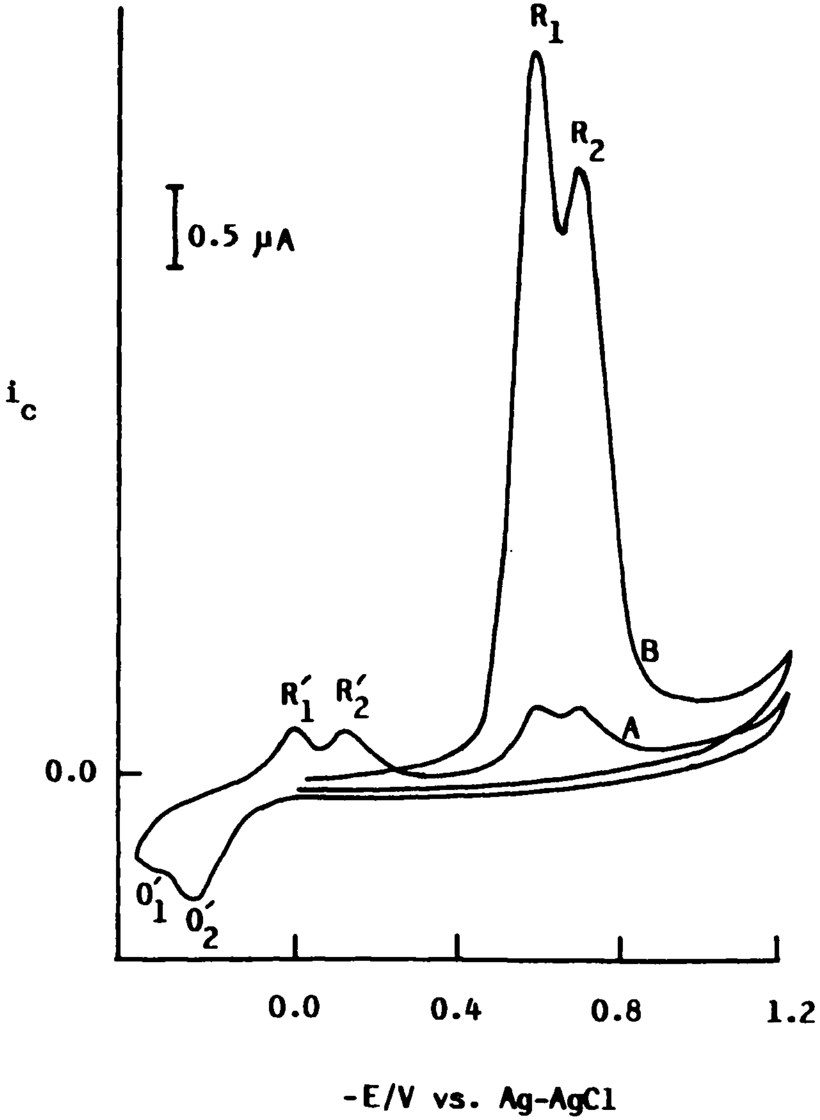

FIGURE 1 Cyclic voltammograms obtained for 1.0 × 10^{-6}M trifluralin at a scan rate of 50 mVs^{-1} (a) without accumulation; (b) 2-min preconcentration time and stirring rate; 400 rpm

electrode surface. When varying the scan rate (v) from 10 to 200 mV s^{-1} the peak intensity increases linearly with the scan rate, confirming an adsorption controlled process.

The effect of pH on the peak potential (E_{pc}) and peak current height (i_{pc}) for the first reduction process of 1.0×10^{-6}M trifluralin was studied by means of linear sweep voltammetry over the pH range 2.0–12.0. As can be seen in Figure 2., the potential of the cathodic stripping peak is shifted to more negative potentials with increasing pH, with change of slope at pH 10.0. At pH > 10.0 there is a little change in E_{pc} with pH. The linear regression equation yielded the relationship $E_{pc} = 0.033$ pH + 0.44 ($r = 0.994$) over the region of pH 2.0–10.0. The peak current has its maximum value at pH 7.0, which was thus chosen for analytical purposes. The peak height was measured from the straight line connecting the minima on both sides of the peak and the value corresponding to supporting electrolyte was subtracted.

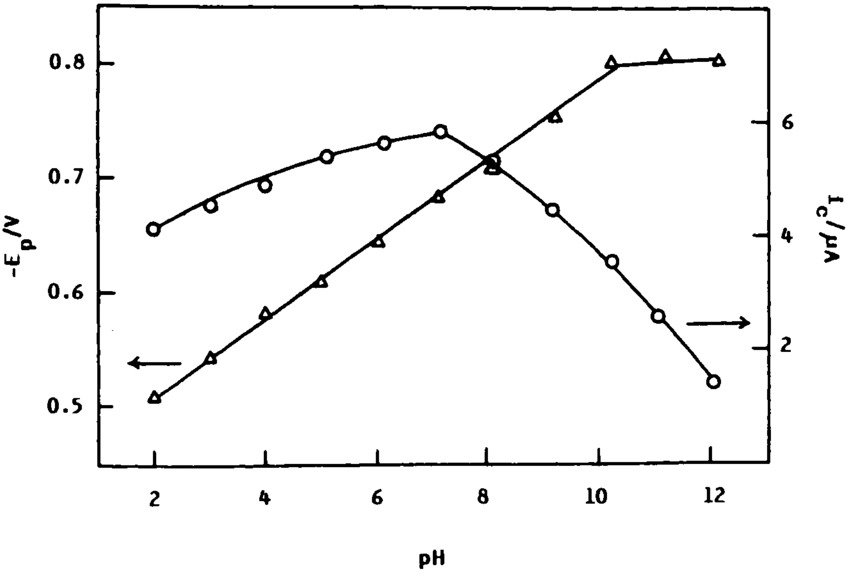

FIGURE 2 Dependence of peak potential and stripping peak current of trifluralin on pH, 1.0×10^{-6}M trifluralin, scan rate; 50 mVs^{-1}and 2-min preconcentration time

Figure 3 shows the dependence of peak current on the preconcentration time at two concentration levels, 2.5×10^{-7}M (a) and 1.0×10^{-6}M (b). The peak current height increases with increasing preconcentration time, indicating adsorption of trifluralin at glassy carbon electrode. For 5-min preconcentration time, an approximately 10-fold enhancement is observed over that attained by conventional solution-phase voltammetry. As a result, submicromolar levels of trifluralin can be easily quantified. The depression of peak current for accumulation period higher than 5 min could be explained in terms of an adsorption equilibrium which is reached as a compromise between the adsorption forces driving the molecules to the surface of the electrode and the possible repulsion interaction of the polar molecules of trifluralin in the adsorbed state, once a given coverage of the electrode has been reached.

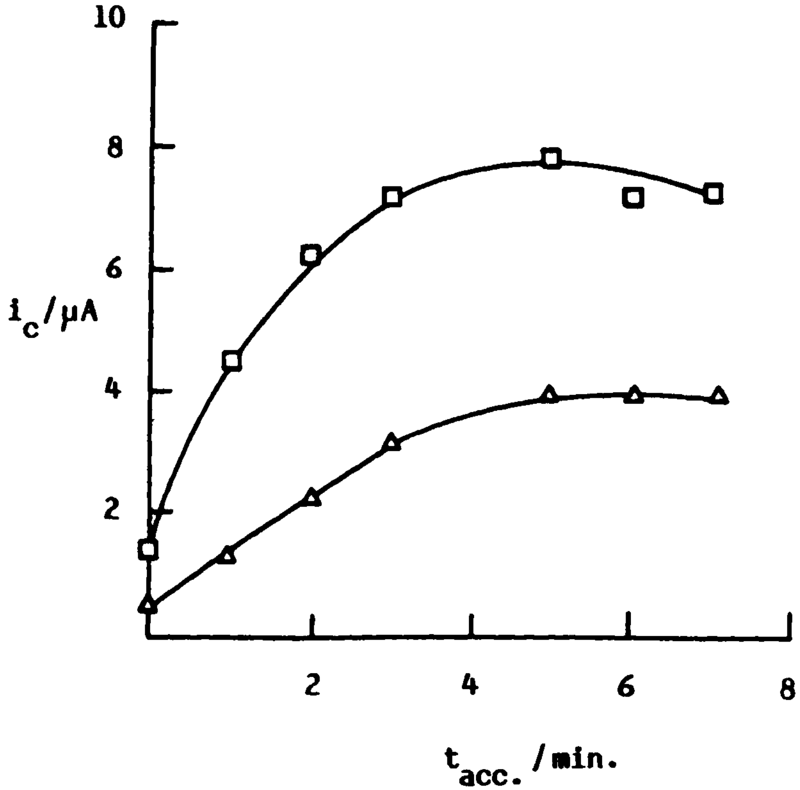

FIGURE 3 Dependence of the peak current on the preconcentration time for 5.0 × 10^{-7}M (a) and 1.0 × 10^{-6}M trifluralin. Preconcentration at open circuit potential with 400 rpm from solution of pH 7.0. Scan rate: 50 mVs^{-1}

The effect of accumulation potential on the stripping peak current was also investigated at pH 7.0 for 1.0 × 10^{-6}M trifluralin after 5-min preconcentration at a potential range from –0.3 to 0.3 V or under open circuit conditions. The accumulation potentials were found to be ofless significance on the degree of accumulation. The stripping peak currents remained almost constant; for this reason the open circuit conditions were used for further study.

Quantitative analysis

Quantitative evaluation is based on the dependence of the peak current on the trifluralin concentration. Figure 4 shows the dependence of the linear sweep stripping peak current on the trifluralin concentration at pH 7.0 following 2 (A) and 5 (B) min preconcentration. As expected for a process limited by interfacial accumulation, deviation from linearity is observed at higher concentration and the linear range is a function of the preconcentration time. After 5-min preconcentration under open circuit conditions in Britton-Robinson buffer of pH 7.0 the calibration curve was linear over the concentration range 2.5×10^{-7}M -1.25×10^{-6}M. The regression equation was $\{i_{pc}$ (μA) = 7.4 C (μM) +0.046, $\rho = 0.994\}$; standard deviations for slope and intercept of the calibration curve were 0.0051 and 0.0043, respectively. Five measurements from five independent samples at concentration of 1.0×10^{-6}M trifluralin gave a relative standard deviation of 3.3 %. The detection limit (estimated as concentration corresponding to the signal to noise ratio of 3),[10] was 2.5×10^{-8}M. This was lowered down to 1×10^{-8}M if higher scan rate ($v = 200$ mVs^{-1}) and stirring rate (2000 rpm) were used. It was found that the differential pulse did not significantly improve the sensitivity attained by the linear scan voltammetry. Moreover, linear sweep mode yielded a better signal to background ratio than differential pulse waveform, at the same time, the scan time can be shortened from minutes to several seconds.

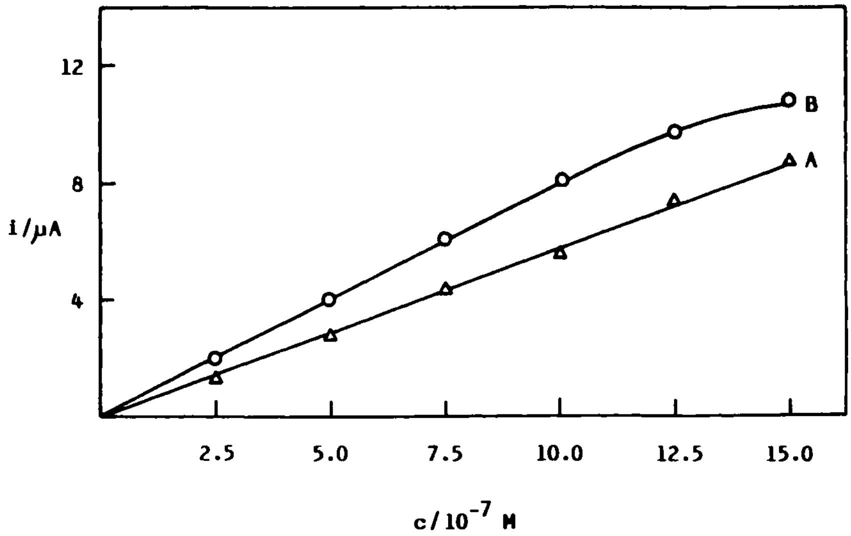

FIGURE 4 Dependence of the peak current on the trifluralin concentration using 2 (a) and 5 (b) min preconcentration. Other condition as in Figure 3

Analysis in soils

The described method was applied for the determination of trifluralin in artificially contaminated soil. Recovery experiments were carried out by spraying a soil sample (25 g) with 50–250 μl of 1.0 × 10^{-5}M trifluralin standard solution. After each addition, the sample was left for 4 h. Extraction of the herbicide was carried out with 100 ml of acetone. The extract was evaporated to dryness and the residue was dissolved in ethanol. An aliquot portion of the dissolved residue was transferred into the voltammetric cell. The stripping peak height at pH 7.0 was recorded (after the removal of oxygen for 10 min) at 5-min preconcentration and stirring rate of 400 rpm. The absence of the matrix effect was indicated from the similar slopes of the above series of standard calibrations (8.0 × 10^{-6} μA 1 mol^{-1}). Hence, the herbicide content was found using the standard addition method. A recovery assay based on five separate determinations performed on artificially contaminated soil containing 4 μg /g of trifluralin showed a mean recovery of 98.3 % with a relative standard deviation of 4.7 %.

In conclusion, the proposed linear-sweep cathodic stripping voltammetric method on a glassy carbon electrode allows the rapid and sensitive determination of trifluralin in soil, and attaining lower detection limit values compared to the polarographic method.[5]The sensitivity of the method might allow the extension of the method to the determination of trifluralin residue in other type of environmental samples.

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