# *The determination of urea and carbamate herbicides using a wall jet electrode*

W. JOHN ALBERY, BERNARD FLEET*, ANA M. OLIVEIRA BRETT†
*Department of Chemistry, Imperial College, London SW7 2AY, UK*

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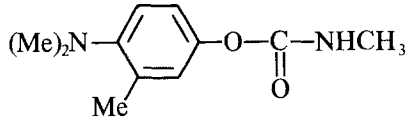
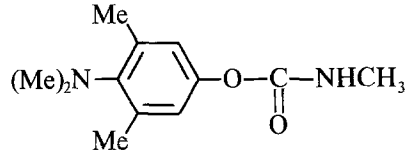
## 1. Introduction

The wall jet electrode [1] is a good electrochemical detector for use in conjunction with high pressure liquid chromatography (HPLC) [2]. It has a small dead space, fast response time and compatible flow rates. In this paper we report the use of a wall jet HPLC system for the separation and determination of eleven different urea and carbamate herbicides. Table 1 gives the names of the herbicides together with their chemical structures.

In previous work Batley and Afgan [3] investigated thirteen different carbamate pesticides using cyclic voltammetry at a glassy carbon electrode. Using their conditions they came to the somewhat gloomy conclusion that only two compounds aminocarb and zectran could be reliably measured:

aminocarb 

zectran 

Anderson and Chesney [4] had more success and were able to measure six different carbamate pesticides; they could also separate a mixture consisting of three separate pesticides. The only compound that is common to our work and theirs is chlorpropham.

## 2. Experimental procedure

The wall jet electrode was of the same design as that of Fleet and Little [2]. The electrode was made of glassy carbon (Plessey) and its radius was 0.252 cm. Using a Milton Roy Instrument Mini-

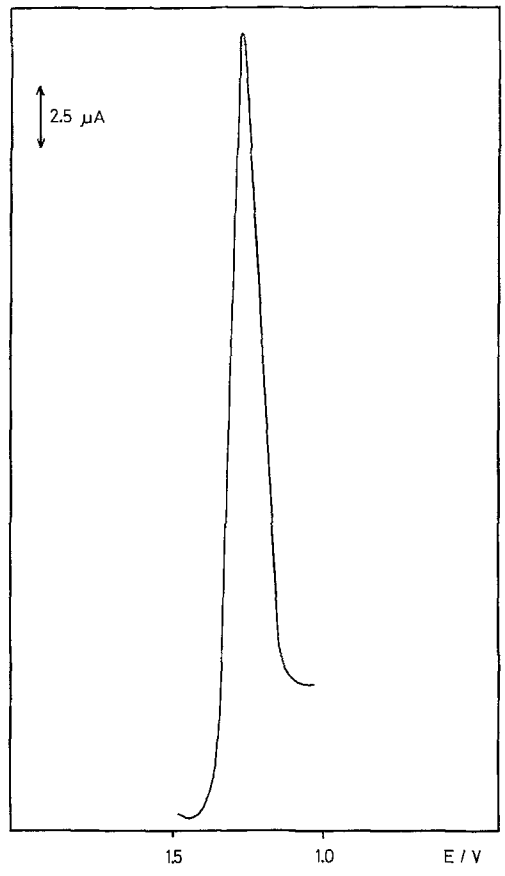



Fig. 1. A typical differential pulse voltammogram for the oxidation of chloroxuron.

* Now at: HSA Reactors Ltd, 44 Fasken Drive, Unit 17, Rexdale, Ontario, M9W SM8, Canada.
† Now at: Departmento de Quimica, Universidade de Coimbro, 3000 Coimbro, Portugal.

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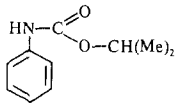
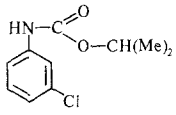
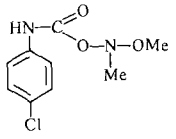
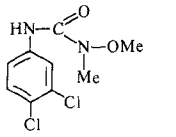
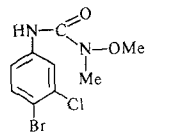
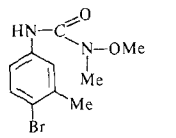
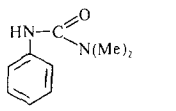
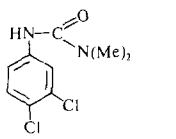
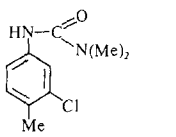
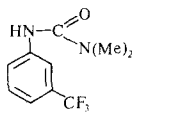
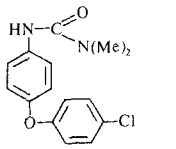
*Table 1. Results for urea and carbamate herbicides*

| *Compound* | *Structure* | *Elution time (min)* | *Calibration plot gradient ($nA\ \mu M^{-1}$)* |
|---|---|---|---|
| Propham |  | 9 | 8.3 ± 0.3 |
| Chlorpropham |  | 12 | 4.7 ± 0.2 |
| Molinuron |  | 8.5 | 7.0 ± 0.1 |
| Linuron |  | 10.5 | 3.7 ± 0.04 |
| Chlorbromuron |  | 12 | 5.8 ± 0.2 |
| Metabromuron |  | 9 | 8.6 ± 0.2 |
| Fenuron |  | 6.5 | 10.2 ± 0.3 |
| Diuron |  | 11.5 | 5.1 ± 0.1 |
| Chlortoluron |  | 8.5 | 7.0 ± 0.1 |
| Fluometuron |  | 9.5 | 5.4 ± 0.1 |
| Chloroxuron |  | 14 | 8.2 ± 0.1 |

pump (396) with pulse dampening a flow rate of $10^{-2}$ cm$^{-3}$ s$^{-1}$ was employed. The reference electrode was Ag/AgCl in 1 mol dm$^{-3}$ KCl and all potentials are reported with respect to this electrode. The potentiostat was a PAR 174. For the separation we used a standard HPLC column (25 cm length and internal diameter of 4.6 mm) packed with Li Chrosorb 10 RP8. This bonded reverse-phase packing material consisted of irregular shaped particles (~ 10 $\mu$m) with the functional group $(CH_2)_7-CH_3$ linked to a C-Si-O-Si backbone. All the herbicides were supplied by Murphy Chemicals and were used without further purification. All other chemicals were of AnalaR grade.

## 3. Results and discussion

Fig. 1 shows a typical differential pulse voltammogram for the oxidation of chloroxuron. The solution contained 50% ethanol by volume, a buffer consisting of 1 mol dm$^{-3}$ each of acetic acid and sodium acetate, and 10 $\mu$mol dm$^{-3}$ of chloroxuron. Of the solutions tested we found that this solvent buffer combination gave the best results. Similar voltammograms were obtained from all of the other compounds in Table 1. The peak potentials ranged from 0.9 to 1.4 V with respect to the Ag/AgCl reference electrode. In the analysis of mixtures of herbicides the electrode potential was set at 1.4 V which is greater than any of the observed peak potentials. Typical results for the flow injection [5] of aliquots of 20 mm$^3$ of solutions of different concentrations of fluometuron are shown in Fig. 2. Reasonable reproducibility and a linear response with concentration is found in the range $10^{-5}$–$10^{-3}$ mol dm$^{-3}$. We estimate the detection limit is $10^{-6}$ mol dm$^{-3}$ in the injected solution. Similar results were found for all of the other compounds in Table 1.

When the detector is coupled to an HPLC column as described in the experimental section, mixtures of different herbicides can be separated and their concentrations determined. Typical results for the two carbamates are shown in Fig. 3.

In Fig. 4 we compare the calibration plots for each compound determined individually and for each compound in the mixture. In each case the gradient from the mixture is some 5% less than the gradient found for the compound on its own. This

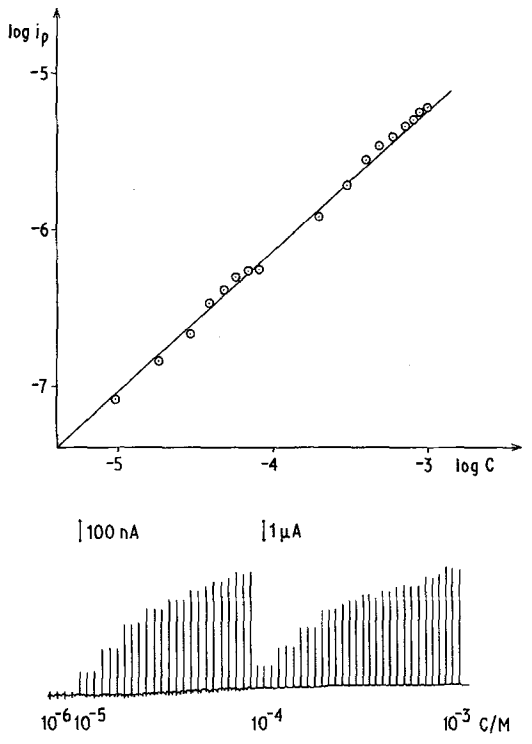



Fig. 2. Typical results for the flow injection of fluometuron. The trace is shown at the bottom of the diagram and the results are plotted as a log/log graph.

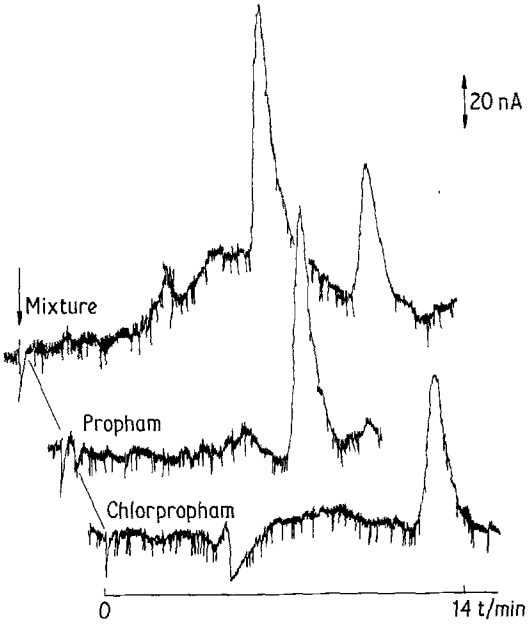



Fig. 3. Typical results for the HPLC wall jet determining the two carbamate herbicides propham and chlorpropham and a mixture of the two. In each case 200 mm$^3$ of a solution containing $10^{-5}$ mol dm$^{-3}$ of herbicides was injected.

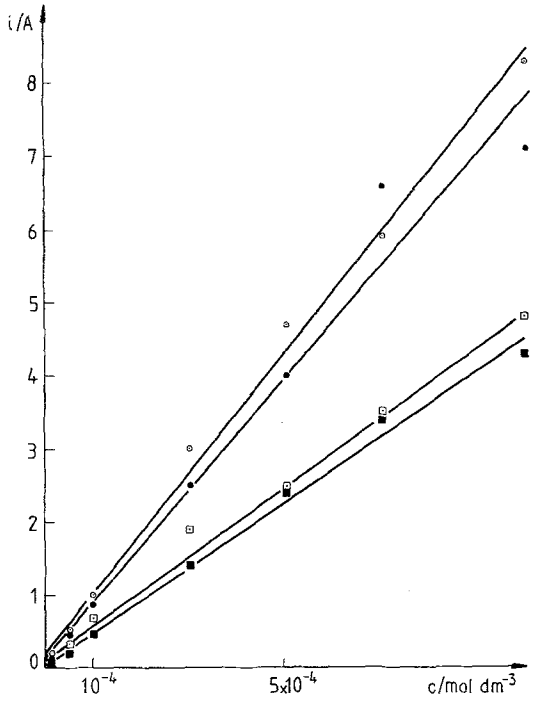



Fig. 4. Typical calibration plots for the two carbamate herbicides obtained from results similar to those in Fig. 3: ⊙ propham; ⊡ chlorpropham; the filled symbols show results from a mixture of the two.

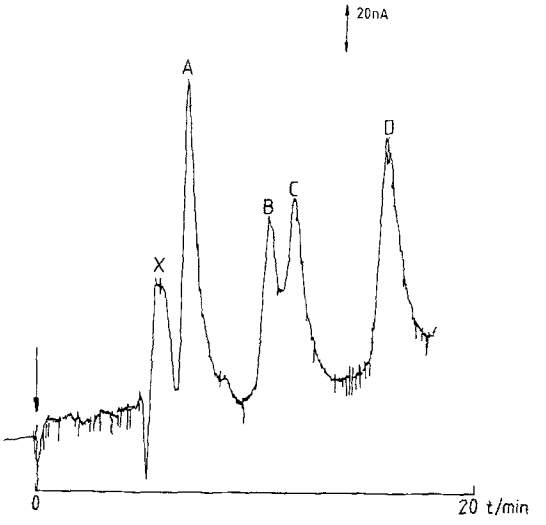



Fig. 5. Typical results for a mixture of four herbicides. A fenuron, B chlortoluron, C diuron and D chloroxuron. Peak X is the solvent front. The mixture contained $10^{-5}$ mol dm$^{-3}$ of each herbicide and 200 mm$^3$ was injected.

behaviour was typical of all the compounds except for chlortoluron, metabromuron and monolinuron. For these compounds there was no significant discrepancy. The same pattern of discrepancy was found when the electrochemical detector was replaced by an ultraviolet detector. We conclude that the reason for this small discrepancy lies in the behaviour of the column rather than in the electrochemical detector.

Typical results for a mixture of four urea herbicides are shown in Fig. 5. The elution times for all the compounds are given in Table 1. It can be seen that complete separation of all eleven herbicides cannot be achieved on this particular column. We also report in Table 1 the slopes of the calibration plots for each compound injected alone onto the column. Our results for chlorpropham are very similar to those of Anderson and Chesney [4].

We have observed that successive scans eventually lead to poisoning of the electrode. For this reason we find that the electrochemical technique will work on a flow system but will not work if one attempts continuous electrolysis. With the flow system in the concentration range studied the number of coulombs passed is not sufficient to inactivate the electrode.

We conclude that by using differential pulse voltammetry together with the given solvent buffer system, the wall jet electrode performs as an adequate electrochemical detector for the HPLC of herbicides.

## Acknowledgement

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