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Note

Determination of phenylurea herbicides by high-performance liquid chromatography with electrochemical detection

GIUSEPPE CHIAVARI* and CECILIA BERGAMINI
Istituto Chimico "G. Ciamician" Università di Bologna, Via Selmi, 2, 40100 Bologna (Italy)
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Substituted phenylureas have been extensively manufactured and used as selective herbicides in agriculture. The need to monitor industrial effluents and to determine traces of such compounds in crops, surface waters and soils has led to the development of new or modified analytical methods.

Chromatographic methods using gas and liquid chromatography have been used for the phenylurea herbicides. However, the polar nature of such compounds, their thermolability and low vapour pressure make difficult the direct analysis by gas chromatography (GC). It is therefore usually necessary to derivatize such compounds, which generally requires an anhydrous medium, consistent reaction times and controlled conditions for removal of excess of the reagent heptafluorobutyric anhydride (HFBA)[1,2]. An indirect method of analysis has also been used, based on hydrolysis of the herbicide to its aniline, derivatization and selective GC with an electron capture detector. However, this procedure is not very specific.

The advent of high-performance liquid chromatography (HPLC) and the use of bonded phases in reversed-phase chromatography has permitted the development of sensitive analytical procedures for the direct determination of organic compounds in water without derivatization. The HPLC of phenylureas has been reported[3,4] using UV detection at 254 nm. Electrochemical detection —the monitoring of changes in current associated with the reduction and/or oxidation of sample component— has proven to be a highly selective and extremely sensitive method for HPLC. Readily oxidizable species such as aromatic amines, phenols and carbonyl compounds can be detected at picomole levels[5–8]. In the present study we have examined the application of this method to the phenylureas.

EXPERIMENTAL

Apparatus

The HPLC system consisted of an Hewlett-Packard 1010 chromatograph with a TW 1515 reciprocating pump (Orlita), a Rheodyne rotary injection valve with 20-μl loop and a Erbasil C_{18}, 10-μm column (250 × 4.6 mm). The electrochemical detector was a Metrohm Model 656 equipped with a glassy carbon working electrode, a glassy carbon counter electrode and a silver–silver chloride electrode, 3 *M* potassium chloride, as a reference. The surfaces of the glassy carbon electrodes were renewed each

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day by mechanical polishing using alumina powder (0.3 μm). A Metrohm 641 potentiostat was employed and the detector output was displayed on a Houston Omniscribe recorder or on a C-R1A Shimadzu data processor.

The eluent was water (triply distilled)–methanol (HPLC) (30:70, v/v) containing an electrolyte (1 g/l lithium perchlorate and 0.05 g/l sulphuric acid). All experiments were done at ambient temperature.

Materials

The herbicide standards were gifts from the Presidi Multizonali di Prevenzione of Bologna and Forlì.

The soil was sprayed with an aqueous solution containing 1 g/l of Dicuran (Ciba-Geigy) which contains 43.6% of active chlortoluron (see Table I). Samples were collected 24 h after this treatment. A 10-g amount of soil was stirred in 50 ml water for 2 h. The pH was then adjusted to 10.5 with 0.1 *M* sodium hydroxide. After centrifugation for 5 min at 1500 *g*, 20 μl of the supernatant were injected for HPLC.

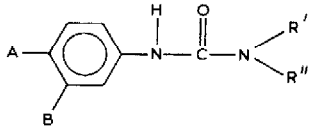
RESULTS AND DISCUSSION

Table I gives the names, structures and retention data for the twelve phenylureas studied. Fig. 1 shows a chromatogram of these compounds; a good separation is obtained for eight herbicides. Figs. 2–4 show the electrochemical responses of the phenylureas as a function of the applied potential. The responses are dependent on the anode conditions, but this does not affect the "relative" response; for a series of compounds. The use of sample concentrations higher than 10^{-5} *M* significantly re-

TABLE I

NAMES, STRUCTURES AND HPLC RETENTIONS (CAPACITY FACTORS, *k'*) FOR PHENYLUREA HERBICIDES

Column: Erbasil C_{18}. Eluent: water–methanol (30:70, v/v) containing 1 g/l $LiClO_4$ and 0.05 g/l H_2SO_4.



Herbicide	*Code*	*A*	*B*	*R'*	*R''*	*k'*
Fenuron	Fe	H	H	CH_3	CH_3	0.86
Metoxyron	Mx	OCH_3	Cl	CH_3	CH_3	1.21
Monuron	Mo	Cl	H	CH_3	CH_3	1.94
Fluometuron	Fm	H	CF_3	CH_3	CH_3	2.02
Monolinuron	Ml	Cl	H	OCH_3	CH_3	2.59
Chlortoluron	Ct	CH_3	Cl	CH_3	CH_3	3.10
Metobromuron	Mb	Br	H	OCH_3	CH_3	3.13
Isoproturon	Ip	$(CH_3)_2CH$	H	CH_3	CH_3	3.36
Diuron	Di	Cl	Cl	CH_3	CH_3	4.38
Linuron	Li	Cl	Cl	OCH_3	CH_3	5.75
Neburon	Nb	Cl	Cl	C_4H_9	CH_3	12.65
Difluron*	Df	Cl	H	$COC_6F_2H_3$	H	13.90

* N-*p*-chlorophenyl-N'-2,6-difluorobenzoylurea.

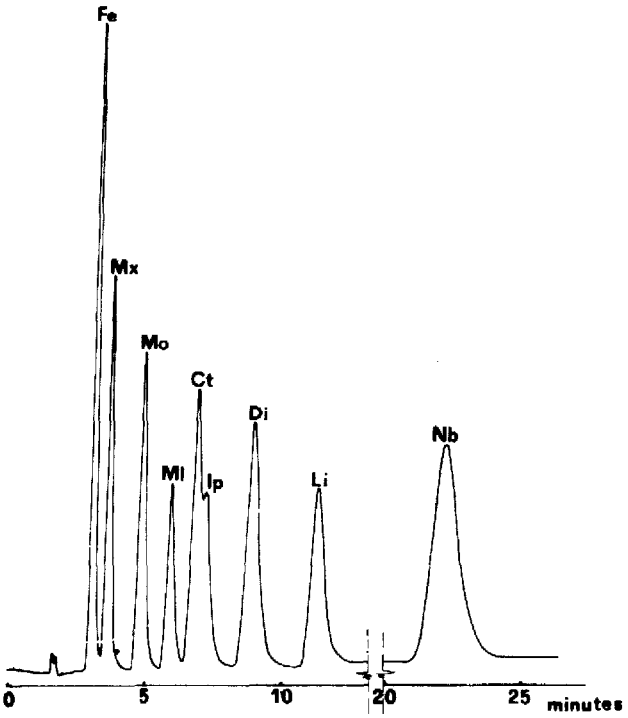


Fig. 1. HPLC separation of nine phenylurea herbicides on Erbasil C_{18} with methanol–water (30:70) containing 1 g/l $LiClO_4$ and 0.05 g/l H_2SO_4 as eluent. Detector potential: 1.30 V.

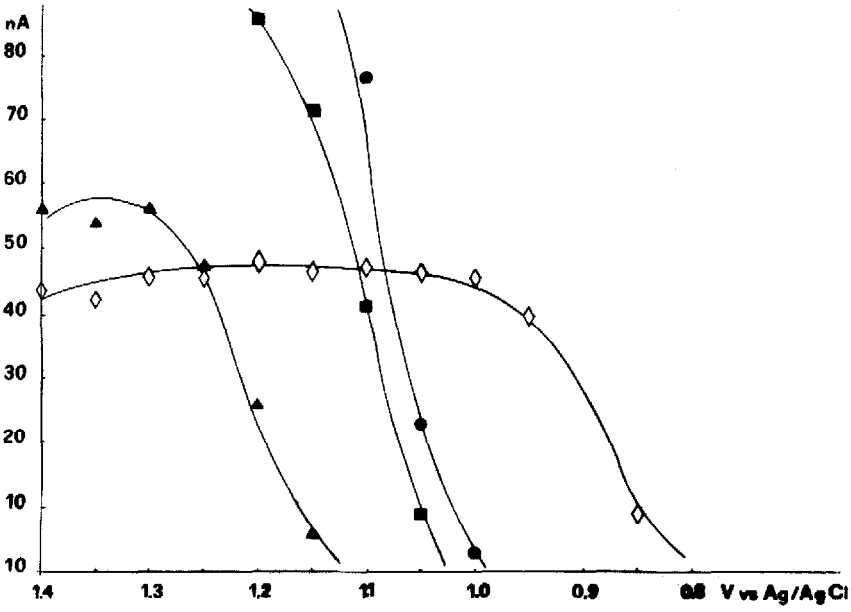


Fig. 2. Dependence of the electrochemical response (nA) on the applied potential (V, *vs.* Ag/AgCl) for 2 nmol each of fenuron (●—●), monuron (■—■), monolinuron (▲—▲) and metoxyron (◇—◇).

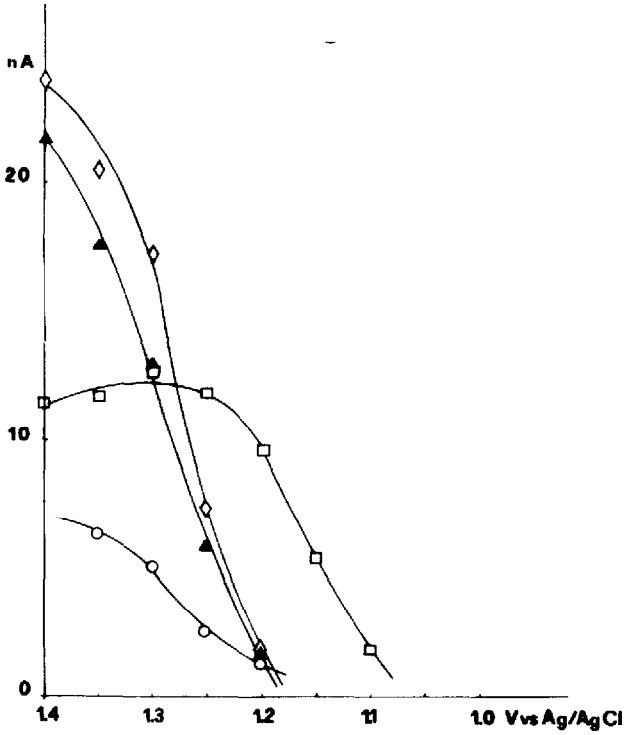


Fig. 3. Dependence of electrochemical response on applied potential as in Fig. 2 for difluron (○—○), fluometuron (▲—▲), neburon (□—□) and linuron (◇—◇).

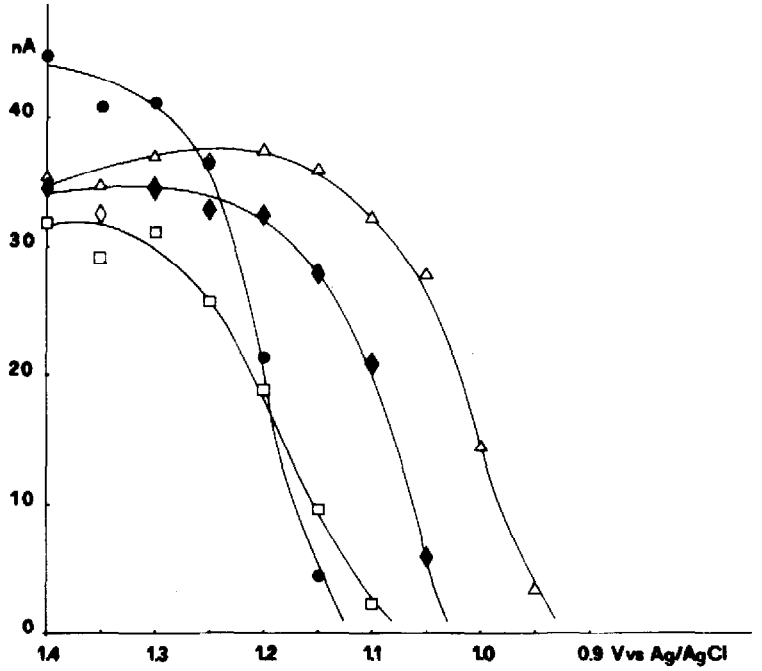


Fig. 4. Dependence of electrochemical response on applied potential as in Fig. 2 for metobromuron (●—●), isoproturon (△—△), chlortoluron (◆—◆) and diuron (□—□).

duces the electrode response after a few injections. In the case of more dilute solutions this problem can be neglected.

The curves for the individual herbicides are significantly different in response and shape. This fact can be usefully employed to vary the detection selectivity by simply changing the oxidation potential. Fig. 5 illustrates an application to a mixture of metabromuron and isoproturon; as reported in Table I, the separation of these two compounds is difficult because of the small difference in k' values and, in our case, still more problematic considering the concentration ratio (10:1). At an oxidation potential of +1.18 V, the two compounds, appear as a single peak with a shoulder on the tail; on lowering the potential, the response of metabromuron decreases and at +1.06 V only isoproturon is detectable. Similarly difficult separations such as monuron/fluometuron or chlortoluron/isoproturon can be solved by taking advantage of their different oxidation curves.

The detection limits for each compound are shown in Table II, based on a signal/noise ratio of $\geqslant 2$. Changes in 2k' or the detector potential will affect these values. In particular, the applied oxidation voltage affects the sensitivity; however, at higher potentials the background noise is increased.

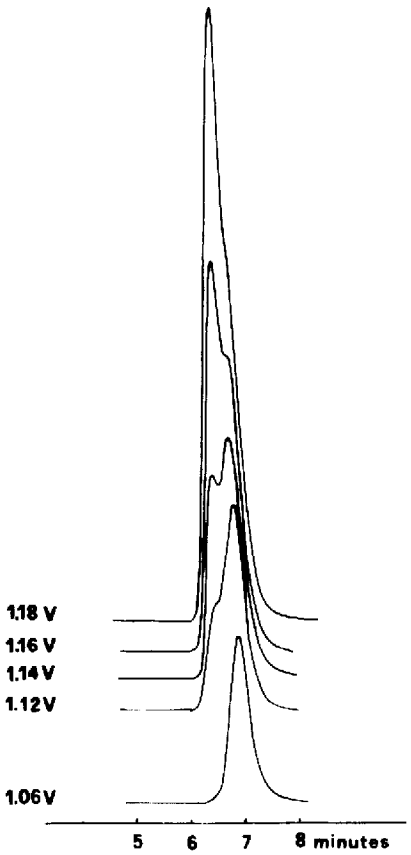


Fig. 5. Chromatogram of the pair metobromuron–isoproturon at various oxidation potentials.

TABLE II

LIMITS OF DETECTION

Based on the quantity required to give a response that is twice the noise level.

Compound (code)	*Limit (pmol)*	*Applied potential (V)*
Fe	7	1.25
Mx	6	1.25
Mo	5	1.25
Fm	18	1.25
Ml	6	1.25
Ct	6	1.25
Mb	6	1.25
Ip	6	1.25
Di	6	1.25
Li	8	1.25
Nb	30	1.35
Df	18	1.35

A plot of peak height *vs.* the amount of sample injected for metobromuron and linuron was linear between 5 and 200 pmol.

Studies are in progress to apply this method to the analysis of phenylureas in environmental samples and to determine whether its selectivity can circumvent the need for time-consuming clean-up procedures in order to remove interfering substances. A preliminary result is shown in Fig. 6; the chromatogram is of a soil sample treated as described in Experimental. The concentration of chlortoluron determined corresponds to a 10^{-5} *M* solution (21 mg per kg soil).

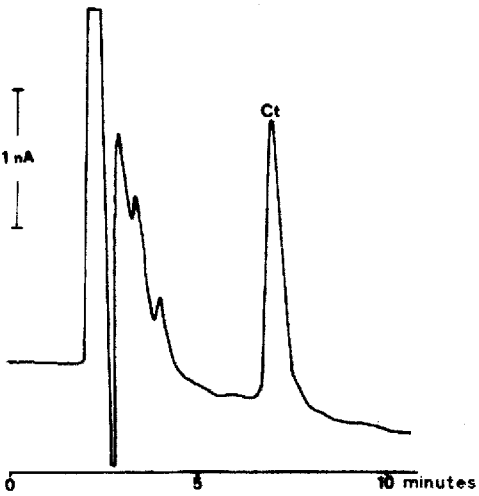


Fig. 6. Chromatogram of chlortoluron-treated soil extract: eluent as in Fig. 1. Detector potential: +11.18 V. Sensitivity: 5 nA f.s.

ACKNOWLEDGEMENT

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