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Determination of linuron in water and vegetable samples using stripping voltammetry with a carbon paste electrode

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ABSTRACT

A carbon paste electrode was used for the electrochemical determination of linuron concentrations in water and vegetable extracts. Optimal conditions were established with respect to electrode activation (electrochemical pretreatment), time accumulation, potential accumulation, scan rate, and pH. The limit of detection achieved with a pre-concentration step was 23.0 $\mu g\,L^{-1}$. Recovery measurements in vegetable extract and natural water samples were in the range of 98–103%, indicating that the proposed electrochemical method can be employed to analyze linuron in these matrices. The determination results were in good agreement with HPLC results.

1. Introduction

Herbicides are the largest group of chemicals used as plant protection agents. One class of herbicides widely used pre- and post-emergence is substituted phenylureas—a less dangerous group of pesticides, given their low toxicity to mammals, high selectivity for specific pests, and good effectiveness at low dosages in common applications [1].

Phenylureas can enter the environment by different pathways, including spray drift, runoff from treated fields, and leaching into groundwater. Although photochemically unstable, phenylureas can persist in water for periods of days or weeks, depending on temperature and pH. Despite their typically low toxicity to mammals, some phenylureas have been reported as carcinogenic in experimental animals.

Phenylurea herbicides selectively control the germination of broadleaf weeds and grasses in all types of crops [2]. Because of their widespread usage, control of residues in ground and surface water is highly important. Phenylurea concentrations on the order of parts per million affect embryonic and neonatal development of fish and aquatic invertebrates [3].

Applied at high frequencies, they are useful as total weed killers, whereas many can be used at low rates for selective weed control in a wide range of crops. Linuron, or 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] (Fig. 1), one of the most important commercial ureas, has good contact activity and the ability to kill emergent weed seedlings [4].

Although most multiresidue methods developed for determination of phenylureas in water, soil, and plant matrices based on chromatography [5], only a few electrochemical analytical studies of this pesticide have been reported. Most of them were based on voltammetric techniques, which have the advantage of usually obviating preliminary separation and purification for the analysis of complex biological materials. Voltammetric methods are therefore particularly useful in the analysis of turbid materials or samples that contain dispersed solid particles. They can be applied without sample pretreatment, a step commonly required in chromatographic analysis that increases both cost and analysis time [6,7].

Linuron determination based on single-sweep derivative polarography was first performed four decades ago, with an approximate limit of detection (LOD) of 2 $g\,L^{-1}$ [5]. More recently, linuron has been determined voltammetrically in water and soil samples using a sepiolite-modified carbon paste electrode, with a LOD of 75 $\mu g\,L^{-1}$ [3]. Also, stripping voltammetric methods using a carbon fiber microelectrode have been proposed for identification (qualitative analysis) of a mixture of carbendazim and linuron in soil samples (although only carbendazim determination has been optimized) [8] and for linuron determination in soil samples (with a LOD of 80 $\mu g\,L^{-1}$) [9].

Some chromatographic methods for linuron determination involve electrochemical detection. The oxidation of two carba-

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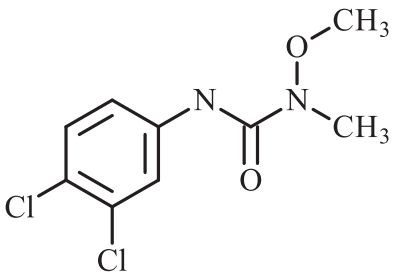

Fig. 1. Molecular structure of linuron.

mates, profam and chlorprofam, and nine ureas, including linuron, has been studied for analytical purposes using electrochemical detection with glassy carbon electrodes. Determination of these herbicides in model samples was performed in a continuous flow system using an amperometric wall-jet detector with and without high-performance liquid chromatographic (HPLC) separation. The LOD for linuron under optimized conditions was 0.24 mg L^{-1} [10]. The determination of a number of pesticides using HPLC, coupled with amperometric detection in model mixtures of benomyl, thiram, linuron, metoxuron, desmedipham, dicuron, lenacil, and fludioxonil dissolved in tap water and beetroot juice has also been performed. Using a glassy carbon electrode at 1.4 V with a thin-layer cell and a wall-jet cell, LODs of 0.17 mg L^{-1} and 0.20 mg L^{-1}, respectively, were measured for linuron [11].

Chromatographic methods for linuron determination using non-electrochemical detectors have also been proposed. For instance, HPLC was employed to determine linuron in potatoes, with estimated recovery values of 89.8% [12], whereas an analytical method based on HPLC with photodiode array detection permitted linuron determination in aqueous soil extracts containing different amounts of organic matter (0.7–11.7%), with a LOD of 10 μg L^{-1} and recovery values from spiked samples in the range of 106.3–116.1% [13]. The latter method was employed to determine linuron adsorption in soils. In addition, a method based on solid-phase extraction (SPE) and liquid chromatography with UV mass spectrometric (MS) or diode array detection (DAD) has been developed for simultaneous determination of ten phenyl- and sulfonylurea herbicides in water, including linuron and one of linuron's most common degradation products. The linuron LODs using HPLC-DAD performed after SPE on UHQ water and river water samples were 18 and 34 ng L^{-1}, respectively [14]. For HPLC-MS performed after SPE on the same samples, the LODs were 15 and 17 ng L^{-1}, respectively. For these two methods, the relative standard deviations ($n = 8$) for linuron determination at 0.1 μg L^{-1} ranged from 13% to 22%.

Carbon paste electrodes (CPE) can be easily prepared and used to detect oxidation or reduction of electroactive compounds adsorbed on their surfaces [15]. Adsorptive stripping voltammetry is a very sensitive electroanalytical technique for the determination of surface active organic compounds and metal complexes in trace amounts [16]. Square-wave voltammetry (SWV), which allows for low LODs and very fast and effective scan rates, can successfully quantify the amount of analyte initially adsorbed [16,17].

In the present investigation, the electrochemical properties of linuron were studied using a new electrochemical method based on the electrochemical activation of a CPE. The proposed method was successfully applied to determine linuron in water and vegetable samples by stripping SWV.

2. Experimental

2.1. Equipments and reagents

All electrochemical measurements were performed with an Autolab PGSTAT12 (Ecochemie, Utrecht, The Netherlands). The experiments were carried out in a three-electrode cell at room temperature (25 ± 1 °C), using a platinum wire as the counter-electrode, Ag/AgCl/KCl (3 mol L^{-1}) as the reference electrode, and a chemically unmodified CPE as the working electrode. The cell was placed in a Faraday cage in order to minimize background noise. The electrochemical techniques SWV and cyclic voltammetry (CV) were applied to investigate the electrochemical behavior of linuron.

A Micronal B-474 pH meter equipped with a combined glass electrode was used for adjusting pH values. Water purified in a Milli-Q system manufactured by Waters was used to prepare the solutions.

The pH values of the linuron solutions were adjusted using 0.2 mol L^{-1} Britton–Robinson (BR) buffer solutions ranging from pH 2 to pH 12. For use as supporting electrolytes, these buffer solutions were prepared by mixing solutions of H_3PO_4, H_3BO_3, and CH_3COOH and adjusting pH by adding suitable amounts of 2.0 mol L^{-1} NaOH. All others reagents were of analytical reagent grade.

Stock solutions of linuron (Sigma–Aldrich; 99.7% purity) were prepared by dissolving this herbicide in an acetonitrile:water (70:30, v:v) mixture.

The samples were analyzed using a Varian 210 analytical HPLC system equipped with a ternary solvent delivery module, an autosampler, and a photodiode array detector. Star WS software (Workstation) was used to measure the peak chromatogram areas. The HPLC column was an RP18 (25 cm × 4.6 mm × 5 μm) reversed-phase column with a small pre-column (2.5 cm × 3 mm) containing the same packing material used to protect the analytical column. Elution was carried out with a methanol:water:acetonitrile (40:40:20, v:v:v) isocratic solvent system for 20 min. The flow rate was 1.0 mL min^{-1} and 20 μL was injected. All chromatographic analyses were performed at 22 °C.

2.2. Construction of the carbon paste electrode

Chemically unmodified carbon paste was prepared by mixing spectroscopic-grade graphite (Sigma–Aldrich; particle size <20 μm) and mineral oil (Sigma–Aldrich) at 80%:20% (w:w). The mixture was homogenized in a mortar for 40 min and inserted into a 1.0 mL plastic syringe. Electrical contact was established via a copper wire.

2.3. Activation and renewal of the carbon paste electrode

The working electrode was placed in a measuring cell filled with 10 mL of BR buffer of known pH. Before each measurement, the buffer-immersed working electrode was activated by applying an anodic potential for 60 s. After electrochemical activation, a known amount of linuron solution was added to the cell containing the buffer solution. Before each voltammogram was recorded, the pesticide was accumulated on the CPE surface by applying an accumulation potential for 60 s under hydrodynamic conditions (magnetic stirring). CV potential scans were recorded starting in the negative direction, in the range from +0.8 V to −0.1 V *vs.* Ag/AgCl, KCl 3 mol L^{-1}. For SWV measurements, the potentials were also scanned in the negative direction from +0.8 V to −0.1 V. Activation and accumulation potentials (+1.3 V for CV, +1.5 V for SWV) were identical for both techniques. Before CPE activation, the electrode surface was renewed and smoothed on a paper sheet.

2.4. Preparation of samples

Known amounts of linuron were added to 10 mL water samples. The resulting solutions were filtered through a Millex filter (0.45 μm pore diameter) ($n = 3$) and directly analyzed using HPLC.