



Pendimethalin determination in natural water, baby food and river sediment samples using electroanalytical methods

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ABSTRACT

This work describes the electroanalytical determination of pendimethalin herbicide levels in natural waters, river sediment and baby food samples, based on the electro-reduction of herbicide on the hanging mercury drop electrode using square wave voltammetry (SWV). A number of experimental and voltammetric conditions were evaluated and the best responses were achieved in Britton–Robinson buffer solutions at pH 8.0, using a frequency of 500 s⁻¹, a scan increment of 10 mV and a square wave amplitude of 50 mV. Under these conditions, the pendimethalin is reduced in an irreversible process, with two reduction peaks at -0.60 V and -0.71 V, using a Ag/AgCl reference system. Analytical curves were constructed and the detection limit values were calculated to be 7.79 µg L⁻¹ and 4.88 µg L⁻¹, for peak 1 and peak 2, respectively. The precision and accuracy were determined as a function of experimental repeatability and reproducibility, which showed standard relative deviation values that were lower than 2% for both voltammetric peaks. The applicability of the proposed methodology was evaluated in natural water, river sediments and baby food samples. The calculated recovery efficiencies demonstrate that the proposed methodology is suitable for determining any contamination by pendimethalin in these samples. Additionally, adsorption isotherms were used to evaluate information about the behavior of pendimethalin in river sediment samples.

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1. Introduction

The intensive use of herbicides, and other classes of chemicals products, in agricultural practices has resulted in serious impacts on the environment, causing an increase in the level of herbicide residues in natural water, soil, river sediments, and foodstuffs [1,2].

Among the herbicides frequently used, pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3-4-xyldine), while the structural formula is presented in Fig. 1, is a dinitroaniline group-containing compound used, as a selective herbicide, to control annual grasses and broad-leaf weeds in the cultivation of corn, potatoes, rice, cotton, soybean, tobacco, peanuts and sunflowers [3,4]. Precise and sensitive analytical methodologies have been developed to monitor pendimethalin residues in different samples, due to this herbicide is considered moderately persistent and bioaccumulative.

The usual analytical methods employed to determine the amount of pendimethalin are based on gas chromatography techniques coupled to either a mass spectroscopy detector [5–8], a nitrogen phosphorous

detector [9], or an electron-capture detector [10,11]. The use of high performance liquid chromatography with an ultraviolet detector [12] and a UV–visible–near infrared spectrophotometer has also been reported [13,14]. Yet, few groups have made electroanalytical determinations or have studied the electrochemical behavior of pendimethalin.

Sreedhar and co-workers [15] have studied the pendimethalin redox process and determined its presence in formulations, grains, soils and spiked-water samples using cyclic voltammetry and differential pulse polarography. Their study was established on the reduction of a nitro group on a dropping mercury electrode, and the results indicate that the proposed procedure assures good precision and accuracy with respect to the determination of pendimethalin. However, the amount of time requested by the analysis, together with the amount of hazardous mercury produced, strongly indicate the necessity of a new development.

Kotoucek and Opraviloká [16] employed fast scan differential pulse voltammetry to evaluate the electrochemical behavior of pendimethalin and other nitroherbicides using a hanging mercury drop electrode in a medium containing 47–49% methanol and 10–20% dimethylformamide. The analytical determination was implemented using adsorptive stripping voltammetry in model samples, combined with an extraction process using acetone. In the work, from 1996, the scan potential was evaluated at 20 mV/s and with a large time of adsorption steps, supplying a detection limit of approximately 1 µg/L, and one application in spiked soil samples, after a time consuming liquid extraction procedure. The

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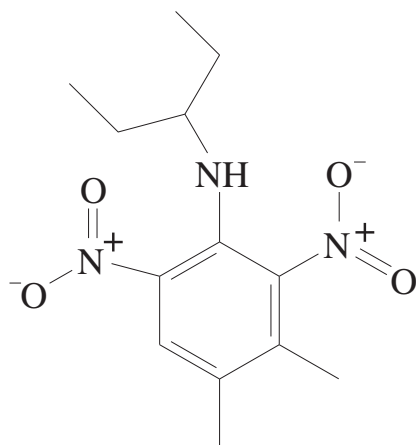


Fig. 1. Structural formula of pendimethalin herbicide.

main limitations here are the long time of analysis and the use of toxic organic solvents.

Hegedús and co-workers [17] developed an enzyme-linked immunosorbent assay (ELISA) for the detection of trifluralin and pendimethalin in surface water samples and vegetable juices. However, the detection efficiency was unsatisfactory because the ELISA system was vulnerable to organic solvents, which are necessary due to low solubility of the pendimethalin in aqueous media.

Recently, Vanková and co-workers [18] employed differential pulse voltammetry, using a silver solid amalgam electrode, in the analytical determination of pendimethalin in drinking water samples, with detection limits around $4.0 \times 10^{-7} \text{ mol L}^{-1}$. This electrode has the drawback of an intense herbicide adsorption onto the electrodic surface, which damages the response reproducibility.

Because pendimethalin is classified as a non-leaching compound, it is characterized by low volatility, low mobility, and low water solubility, and thereby presents a high persistence in soil and river sediments, with a half-life that depends on the properties of the soil or sediments [19,20]. Still, very few studies have reported on the adsorption of this herbicide in soil or river sediments. The studies that have been performed were conducted using high performance liquid chromatography with a diode array detector [21] or gaseous chromatography with an electron capture detector [22], with each method requiring further cleanup by solid-phase extraction prior to instrumental analysis [23].

The use of voltammetric techniques to evaluate the adsorption of pendimethalin in the soil and sediments is very rare. Therefore, the aim of this work was to develop an electroanalytical methodology to pendimethalin determination in natural water, river sediment and baby food samples based on its electroreduction on a hanging mercury drop electrode (HMDE) using square wave voltammetry (SWV). SWV was applied for herbicide detection because of its extreme sensitivity [24–27].

The topic of herbicide determination in commercial baby food is of particular interest, considering that various herbicides are widely used in several stages during the cultivation and storage of the principal products found in baby food, e.g., apple, papaya, orange juice and rice. For babies (6 to 12 months) who consume it, baby food can become the dominant source of unsafe levels of herbicides in their bodies. To prevent this from occurring, it is necessary to develop a simple, sensitive and reliable methodology to analyze herbicides residues, such as pendimethalin, in commercial baby food.

2. Experimental

2.1. Reagents and apparatus

All voltammetric measurements were performed on a PGZ 402 Voltalab potentiostat from Radiometer Analytical coupled to Volta-

master 5.06 software. A polarographic station (model MDE 150) from Radiometer Analytical, containing an Ag/AgCl/KCl 1.0 mol L^{-1} as reference electrode, a platinum plate as auxiliary electrode and mercury as working electrode, was operated in HMDE mode. The HMDE surface, with an area of 0.012 cm^2 , was renewed after each measurement. A new drop was automatically formed by nitrogen pressure in the system after dislodging the old drop and extruding more triple-distilled mercury.

A Metron model 682 pH-meter equipped with a 3.0 mol L^{-1} Ag/AgCl/KCl-glass combined electrode was used for adjusting pH values. Water, purified by a Milli-Q system from Millipore Corporation, was used to prepare all the solutions.

The centrifugation procedure in the river sediments and babyfood samples was performed using a Fanem centrifuge model 206 which present a swinging bucket rotor with capacity of 12 tubes of the $10 \times 500 \text{ mm}$ and a maximum speed of the 15,000 rpm.

All chemicals were of analytical-reagent grade. Pendimethalin herbicide was provided by BASF Chemical Company – Brazil, with a purity of 98.0%. A $1.9 \times 10^{-2} \text{ mol L}^{-1}$ stock solution of herbicide was prepared using ethanol denatured from Baker for HPLC analysis with 99.7% of purity.

2.2. Optimization of the procedure

All measurements were carried out under ambient conditions. The appropriate solutions were transferred into the electrochemical cell and the optimization of the analytical procedure for SWV was carried out. For this, a systematic study of the experimental parameters that affect the responses, such as the pH of the medium, the pulse potential frequency (f) related to total pulse duration, the amplitude of the pulse (a) and the height of the potential step (ΔE_s) or scan increment were evaluated. All parameters were optimized in relation to the maximum value of the peak current and the maximum selectivity (half-peak width).

Before each experiment, a stream of N_2 was passed through the solution for 10 min to remove all oxygen, which can interfere with voltammetric measurements on an HMDE.

The working electrode was then placed in the measuring cell, which contained 8.5 mL of an electrolyte support solution and 1.5 mL of ethanol denatured, which correspond to 15% of the total volume in the electrochemical cell. This organic solvent was used to ensure the solubility of pendimethalin in an aqueous medium. A known concentration of pendimethalin was added to this cell, after which the experimental and voltammetric parameters were studied. For the actual measurements, several support electrolytes were initially evaluated, with the best results being obtained in 0.1 mol L^{-1} BR buffer.

After optimizing the voltammetric parameters, analytical curves were obtained in pure electrolyte solutions by the standard addition method. The standard deviation of the mean current, measured at the reduction potential of pendimethalin for 10 voltammograms of the blank solution in pure electrolytes (S_b), together with the slope of the straight line of the analytical curves (s) were used in the determination of the quantification and detection limits (QL and DL , respectively), according to guidelines recommended by IUPAC [28,29].

The recovery experiments were done in order to attest the methodology's efficiency. These experiments were carried out by adding a known amount of pendimethalin to the supporting electrolytes followed by standard additions from the pendimethalin stock solutions and plotting the resulting analytical curves. All measurements were performed in triplicate. The recovery efficiencies (%R) were calculated considering the ratio between the value of the concentration obtained by extrapolating the analytical curves of the corresponding spiked samples and the concentration previously added [30].

The precision and accuracy of methodology were tested with different standard solutions of pendimethalin and the relative standard deviations (RSD) were calculated, considering the standard

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