



A greener and highly sensitive flow-based procedure for carbaryl determination exploiting long pathlength spectrophotometry and photochemical waste degradation

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ABSTRACT

An environmentally friendly analytical procedure with high sensitivity for determination of carbaryl pesticide in natural waters was developed. The flow system was designed with solenoid micro-pumps in order to improve mixing conditions and minimize reagent consumption as well as waste generation. A long pathlength (100 cm) flow cell based on a liquid core waveguide (LCW) was employed to increase the sensitivity in detection of the indophenol formed from the reaction between carbaryl and p-aminophenol (PAP). A clean-up step based on cloud-point extraction was explored to remove the interfering organic matter, avoiding the use of toxic organic solvents. A linear response was observed within the range 5–200 $\mu\text{g L}^{-1}$ and the detection limit, coefficient of variation and sampling rate were estimated as 1.7 $\mu\text{g L}^{-1}$ (99.7% confidence level), 0.7% ($n=20$) and 55 determinations per hour, respectively. The reagents consumption was 1.9 μg of PAP and 5.7 μg of potassium metaperiodate, with volume of 2.6 mL of effluent per determination. The proposed procedure was selective for the determination of carbaryl, without interference from other carbamate pesticides. Recoveries within 84% and 104% were estimated for carbaryl spiked to water samples and the results obtained were also in agreement with those found by a batch spectrophotometric procedure at the 95% confidence level. The waste of the analytical procedure was treated with potassium persulphate and ultraviolet irradiation, yielding a colorless residue and a decrease of 94% of total organic carbon. In addition, the residue after treatment was not toxic for *Vibrio fischeri* bacteria.

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1. Introduction

Carbamates are one of the most important classes of pesticides. Carbaryl (1-naphthyl-N-methyl carbamate) is a broad-spectrum insecticide, used to control more than 100 kinds of pests in crops such as beans, bananas, potatoes and domestic vegetables [1]. However, this substance inhibits the cholinesterase enzyme, impairing the functions of the central nervous system and can cause nausea, vomit, broncho-constriction, blurred vision, convulsions, coma and respiratory failure, in addition to its teratogenic characteristics [2].

Several procedures have been described in the literature for the analysis of carbaryl in different matrices [3–7], mainly based on chromatographic separation [8–11]. The 8318 reference method, recommended by the United States Environmental Protection Agency (EPA) for the determination of N-methylcarbamates in soil, water and wastes, for example, is based on high performance liquid chromatography (HPLC) with fluorimetric detection after post-

column derivatization. Before analysis, the analyte is extracted with a mixture of ethylene glycol, methanol and acetonitrile [1].

The spectrophotometric determination of carbaryl can be performed using p-aminophenol (PAP), p-N,N-dimethylphenyl-enediamine dihydrochloride or 1-amino-2-naphthol-4-sulphonic acid as chromogenic reagents, forming a product with absorption maximum between 600 and 700 nm. For analyte extraction from water samples, up to 200 mL of chloroform are used per determination [3]. Other spectrophotometric procedures are based on diazotization with trimethylaniline (TMA) in a micellar medium containing sodium dodecyl sulfate [2]. The anionic surfactant was used to dissolve TMA and provides a suitable medium for the coupling reaction with 1-naphthol. Later, the same anionic surfactant was used in an acid-induced cloud-point extraction coupled to derivatization with 2-naphthylamine-1-sulfonic acid (ANSA) reagent for determination of carbaryl residues in waters and vegetables. The proposed method showed good analytical features, including low detection limit, but a large amount of concentrated HCl was used (5.0 mL per sample) [12]. Alternatively, a procedure based on double cloud-point extraction for determination of carbaryl in natural waters was proposed. The analyte was separated from the matrix using Triton X-114 in an alkaline medium in

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order to avoid the use of toxic organic solvents. Cloud-point pre-concentration of the indophenol product was explored to increase sensitivity and to improve the detection limit [13].

The spectrophotometric determination of carbaryl has also been implemented in flow systems [6,14–17]. A single-line manifold based on the reaction of carbaryl with diazotized sulfanilic acid in alkaline medium was used in the first work described in the literature [15]. A linear response was observed within the range 0.1–40 mg L⁻¹ carbaryl, with a detection limit and coefficient of variation estimated as 0.08 mg L⁻¹ and 3.8%, respectively. Other flow-based procedures have exploited the reaction of the hydrolyzed carbaryl with p-aminophenol in an alkaline medium, forming indophenol blue, with maximum absorption at 585 nm [14–17]. The carbaryl extraction step consumes large amounts of reagent—2.5 g of anhydrous sodium sulfate, 60 mL of methylene chloride and 10 mL of sodium hydroxide per determination [15] or 10 mL xylene, followed by back-extraction of the α -naphtholate with 0.2 mol L⁻¹ NaOH [16].

Recently, a flow procedure based on chemiluminescence [18] was developed, exploiting the oxidation of the pesticide by Ce(IV) in a nitric acid medium containing rhodamine 6G as a sensitizer. Solid-phase extraction was used to concentrate and separate the analyte from the matrix, followed by elution using 5 mL of a 1:1 ethyl acetate: n-hexane solution. The eluent was collected and evaporated to dryness under a nitrogen stream. Ethanol was directly added to the residue and the amount of analyte was then determined. A new solvent extraction and concentration procedure using microchip technology was based on thermal lens spectroscopy [19]. After pesticide hydrolysis in alkaline medium and coupling of 1-naphthol with diazotized trimethylaniline, the reaction product was extracted with toluene as a colored azo-dye.

Sensitivity in spectrophotometry can be enhanced by increasing the optical path, hence a larger amount of absorbing species is available to interact with the radiation beam. However, for cells fabricated with conventional materials, the increase in the optical path is limited by the excessive attenuation of the radiation beam, also demanding higher sample volumes [20]. Liquid core waveguides (LCWs) with capillary dimensions have been used to circumvent these drawbacks. The capillary tubes are constructed with a polymer with refractive index lower than that of water (e.g. Teflon AF family) or by fused silica covered with this material. In this way, radiation incident at a suitable angle in the liquid core is constrained inside the waveguide by total reflection that occurs between the liquid and the tube wall [21,22]. These devices have been used for the determination of species at nanomolar level in environmental samples [23–25], including gaseous analytes [26] and also for measurements based on turbidimetry [26,27] or luminescence [22].

In this work, an improved flow-based procedure for determination of carbaryl in natural waters is described. The procedure is based on the alkaline hydrolysis of carbaryl to 1-naphthol which is coupled to the oxidized form of PAP. The flow system was designed with solenoid micro-pumps to minimize reagent consumption and long pathlength spectrophotometry (LPS) was explored to increase sensitivity. The clean-up step, often carried out with organic solvents, was replaced by a simple, fast and environmentally friendly cloud-point extraction. The waste was photochemically decomposed and characterized before toxicity tests with the marine bacteria *Vibrio fischeri*.

2. Experimental

2.1. Apparatus

The flow system was constructed with four solenoid micro-pumps of 12 (P₁, P₂ and P₃) and 7 μ L (P₄) nominal volume per pulse (Biochem Valve Inc., Boonton, NJ, USA; model 090SP), a pair

of three-way solenoid valves (NResearch, West Caldwell, NJ, USA), 0.7 mm i.d. polyethylene tubes and a Perspex joint. A Pentium I microcomputer was used for system control and data acquisition. The solenoid micro-pumps and valves were controlled through a parallel port of the microcomputer by using a power drive based on a ULN2803 integrated circuit. Spectrophotometric measurements in dual-wavelength mode (585 and 750 nm) were carried out with a multi-channel CCD spectrophotometer (Ocean Optics, Dunedin, FL, USA; model USB2000) coupled to a tungsten-halogen light source (Ocean Optics; model LS-1). Optical fibers (100 or 600 μ m) were used to transmit the radiation. A 100 cm optical path (250 μ L internal volume, 0.55 mm i.d.) flow cell (Ocean Optics; model LPC-1) was also employed. The control software was developed in Visual Basic 6.0 (Microsoft, Redmond, WA, USA) and the software supplied by the manufacturer of the multi-channel spectrophotometer was used for data acquisition.

The photo-reactor used for waste degradation was similar to the previously described [28]. It consists of a 400 W low-pressure mercury lamp, obtained from a common street lightning fluorescent lamp (Philips) by removing the external glass bulb. The socket of the lamp was fixed at the ends of a PVC cylindrical tube (10.2 cm i.d., 60 cm length) commonly used in construction field to transport sewage. The lamp was powered by an appropriate power supply (Serwal RIM426B, 220 V) and shows a continuous emission spectrum, predominantly in the visible and emission lines typical of mercury vapor at 254, 313 and 366 nm. The waste generated was positioned in a beaker at 10 cm from the lamp and kept under constant agitation.

UV–vis absorption spectra were obtained with a spectrophotometer (HITACHI, Schaumburg, IL, USA; model U-3000), equipped with a quartz cuvette (1 cm). Total organic carbon was determined using a SHIMADZU TOC-5000A analyzer (Santa Clara, CA, USA). A SHIMADZU LC-20 AT liquid chromatograph with UV–vis detector was used in characterization studies of the generated waste. In toxicity tests, a luminometer MICROTOX 500-B-7120 (Carlsbad, CA, USA) with integrated control and measurement units was used.

2.2. Reagents and solutions

All solutions were prepared with analytical grade chemicals and distilled and deionized water. The reference solutions were prepared in the range 5.0–400.0 μ g L⁻¹ (2.5×10^{-8} to 2.0×10^{-6} mol L⁻¹) carbaryl (Sigma–Aldrich, St. Louis, MO, USA) by dilution of a 7.5×10^{-5} mol L⁻¹ stock solution, prepared in 5% (v/v) ethanol (Merck, Darmstadt, Germany).

The reagents were 4.6×10^{-5} mol L⁻¹ p-aminophenol (Sigma–Aldrich, R₁) and 2.0×10^{-4} mol L⁻¹ potassium metaperiodate (Merck, R₂) solutions prepared by dissolving appropriate amounts of the chemicals in water. A 1.0×10^{-2} mol L⁻¹ sodium hydroxide (Merck) solution was employed as carrier.

Carbamate pesticides (aminocarb, bendiocarb, carbofuran, pirimicarb and propoxur) were obtained from Sigma–Aldrich. Solutions at 1.2 – 9.9×10^{-7} mol L⁻¹ concentrations were prepared in water.

River and lake water samples were collected in the state of São Paulo, Brazil. Samples were filtered through a 0.45 μ m cellulose acetate membrane and preserved at -4°C , being stabilized at ambient temperature immediately before analysis.

2.3. Flow diagram

The flow manifold, shown in Fig. 1, was operated according to the switching course of the active devices described in Table 1. The binary sampling approach [29] was adopted for solutions handling. Low volume aliquots of the solutions were inserted in tandem into the analytical path, generating a sampling profile that was repeated

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