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Note

Determination of carbaryl by high-performance liquid chromatography with electrochemical detection

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(First received November 25th, 1987; revised manuscript received February 2nd, 1988)

Carbaryl (1-naphthyl-N-methylcarbamate) is an extensively used broad-spectrum insecticide and the exposure to this compound has been associated with toxicity in both domestic animals and man. Numerous high-performance liquid chromatographic (HPLC) methods have been developed for the determination of carbaryl and its hydrolysis product 1-naphthol using UV¹⁻⁹, visible¹⁰ or fluorescence¹¹⁻¹⁴ detection. In all except two^{2,3} a reversed-phase HPLC system was used. Carbaryl readily undergoes alkaline hydrolysis to yield methylamine and 1-naphthol. The liberated methylamine forms an intense fluorophore with *o*-phthalaldehyde and mercaptoethanol, and the resulting fluorophore has been detected on-line with a fluorescence detector^{11,13,14}. On the other hand, the analytical separation of mono- and dihydroxynaphthalenes including 1-naphthol by HPLC with electrochemical detection (ED) was achieved by Chiavari *et al.*¹⁵, but carbaryl was not measured by this technique. In this paper, a procedure for the determination of carbaryl by HPLC with ED is described.

EXPERIMENTAL

Chemicals

Carbaryl was obtained from Wako Junyaku (Osaka, Japan). 1-Naphthol and 2-naphthol were purchased from Tokyo Kasei (Tokyo, Japan) and purified by sublimation. All solvents were of HPLC grade (Wako Junyaku).

High-performance liquid chromatography

The apparatus used was a Model 5A high-performance liquid chromatograph (Shimadzu, Kyoto, Japan) with a detector system consisting of a thin-layer flow-through electrochemical cell with glassy carbon as the working electrode and a silver-silver chloride reference electrode (Type VMD 101; Yanagimoto, Japan). A stainless-steel reversed-phase HPLC column (250 × 4.6 mm I.D.) was prepared with Develosil ODS (5- μ m particle size) (Nomura Chemical, Japan). Elution was carried out with acetonitrile-acetic acid-0.5 M potassium chloride (50:1:49) at a flow-rate of 1.0 ml/min. All separations were performed at 25°C and the cell potential was maintained at +0.75 V vs. a silver-silver chloride reference electrode. If the sensitivity of the working electrode decreased, the surface was renewed by polishing it with alumina powder (0.3 μ m) to regenerate the electrode.

Samples

After an aerial spray, deposited carbaryl was collected for 1 h on a filter-paper (30 cm in diameter). The paper was washed with 100 ml of acetone, the solution was evaporated to dryness and the residue was dissolved in 1.0 ml of water.

Procedure

A 1-ml sample solution was made alkaline with 0.20 ml of 0.2 *M* sodium hydroxide and allowed to stand for 10 min at 25°C. After acidification by adding 0.25 ml of 0.2 *M* hydrochloric acid containing 2-naphthol as an internal standard, an aliquot was introduced into the HPLC system with a Model 7125 loop injector (Rheodyne, Cotati, CA, U.S.A.).

RESULTS AND DISCUSSION

Fig. 1 shows chromatograms obtained from a standard solution and a sample solution. There are two distinct peaks with retention times of 8 and 9 min, corresponding to 2-naphthol and 1-naphthol, respectively, and the separation factor α (1-naphthol/2-naphthol) was 1.13. The dotted line in Fig. 1A corresponds to the peak of carbaryl, which shows no ED response. The effect of the applied potential on the peak heights of 1-naphthol and 2-naphthol was determined by changing the oxidation potential in 0.05-V increments from +0.30 to +1.10 V. The resulting hydrodynamic voltammogram is presented in Fig. 2.

1-Naphthol proved to be more easily oxidized than 2-naphthol. The applied potential was set at +0.75 V vs. a silver-silver chloride reference electrode for measuring 1-naphthol, and 2-naphthol was used as an internal standard. An applied potential of +0.75 V was considered to be adequate for keeping the background noise and interference from co-existing electroactive compounds to a minimum and yet obtain a sufficient sensitivity to detect low concentrations of 1-naphthol. Carbaryl

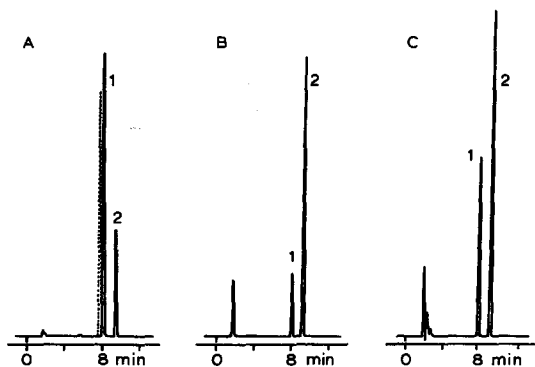


Fig. 1. Liquid chromatographic separation of 1-naphthol (2) with 2-naphthol (1) as an internal standard. Chromatographic conditions: column, 250 \times 4.6 mm I.D. filled with 5- μ m Develosil ODS; column temperature, 25°C; mobile phase, acetonitrile-acetic acid-0.5 *M* potassium chloride (50:1:49); flow-rate, 1.0 ml/min; injection volume, 10 μ l. (A) Standard solution containing 1.0 μ g/ml of 2-naphthol and 0.4 μ g/ml of 1-naphthol, UV detection (267 nm); dotted line, carbaryl. (B) The same standard solution as in A, voltammetry (+0.75 V). (C) Sample solution corresponding to 0.6 μ g/ml of carbaryl, voltammetry (+0.75 V).

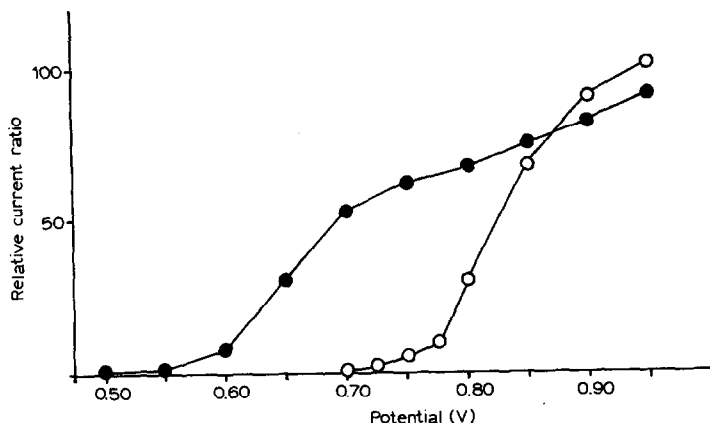


Fig. 2. Dependence of the electrochemical response on the applied potential (V vs. Ag-AgCl) for (●) 1-naphthol and (○) 2-naphthols.

samples may contain 2-naphthylcarbamate as a contaminant, derived from impure 1-naphthol containing 2-naphthol³, but, as shown in Fig. 2, the response of 2-naphthol is much lower than that of 1-naphthol at +0.75 V. Hence the use of 2-naphthol as an internal standard causes no problems. When the determination of 2-naphthol is very important, it is recommended that it is measured at higher potentials.

It is known that carbaryl is very unstable to hydrolysis in alkaline solution^{3,8,11,14}. Therefore, suitable hydrolysis conditions for carbaryl were examined. The extent of the hydrolysis was evaluated by HPLC with UV detection (267 nm). As a result, the procedure described above was established and the calibration graph for 1-naphthol was linear in the range 40–200 ng/ml (correlation coefficient = 0.9972). The reproducibility of the procedure was determined using standard solutions containing 50 and 100 ng/ml of carbaryl and 0.2 M hydrochloric acid containing 2.0 µg/ml of internal standard. As a result, the coefficients of variation were 4.2% ($n = 5$) and 3.6% ($n = 5$). The detection limit was calculated to be less than 1 ng/ml for 1-naphthol (1.5 ng/ml as carbaryl) with a 20-µl injection.

The described method has been successfully applied to the determination of carbaryl deposited on the ground by spraying it from a helicopter. An example of HPLC separation is illustrated in Fig. 1C. There were no interfering peaks from co-existing compounds in the sample solution. The proposed method proved to be satisfactory with respect to sensitivity, selectivity and simplicity.

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