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Native *vs* photoinduced chemiluminescence in dimethoate determination

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ABSTRACT

The determination of dimethoate using either its native chemiluminescent (CL) properties or its photoinduced chemiluminescence obtained by irradiation with a 15 W low-pressure mercury lamp was studied. Thereby, two flow injection systems (FIA) with and without irradiation were exhaustively optimized and their analytical characteristics studied. Better sensitivity and selectivity was found in absence of irradiation, due to the enhancing effect of hexadecylpyridinium chloride (HPC), which acted as a sensitizer. In the developed FIA-CL system, the alkaline hydrolysis of dimethoate with NaOH was performed on-line in presence of HPC. The oxidation of the product of hydrolysis with Ce(IV) in hydrochloric medium induced chemiluminescence. The method provided a limit of detection of only 0.05 ng mL^{-1} without any pre-treatment. However, the combination with solid phase extraction allowed the removal of some potential interferents as well as the preconcentration of the pesticide. Finally, the developed method was successfully applied to natural waters with recoveries between 95 and 108%.

1. Introduction

Dimethoate (O,O-dimethyl-S-methylcarbamoyl methylphosphorothioate) (Fig. 1) is a systemic and contact broad-spectrum insecticide and acaricide, used against numerous crops as well as to control houseflies. It belongs to the organophosphate family and, as most of these pesticides, is moderately toxic and readily absorbed through the skin and lungs, acting as a cholinesterase inhibitor, an enzyme essential for normal nerve impulse transmission. It is enzymatically converted in the intestine wall and liver enabling desulfuration to its oxon-derivative omethoate (O,O-dimethyl-S-methylcarbamoyl methylthiophosphate) causing enhanced neurotoxicity [1]. Hence, it is highly toxic to fish and aquatic invertebrates. The World Health Organization (WHO) has set an Acceptable Daily Intake (ADI) value for dimethoate of 0.002 mg kg^{-1} bodyweight. Dimethoate is very soluble in water. It hydrolyses very slowly at pHs between 2 and 7 and it is not photodegraded by sunlight; consequently it is persistent in the aquatic environment.

The most usual methods of determining dimethoate are based on gas chromatography (GC) coupled with a nitrogen–phosphorus detector [2,3], electron ionization mass spectrometry [4,5] or flame photometric detection [6,7]. Nevertheless, liquid chromatography/mass spectrometry (LC/MS) is the most advantageous approach for the analysis of polar, non-volatile or thermally labile compounds as dimethoate. The liquid separation combined with electrospray ionization followed by tandem-mass spectrometric detection (LC–ESI-MS/MS) [8–10] has been used to overcome the above-mentioned drawbacks. A further advance in the analysis with LC/MS/MS is the use of the isotope dilution method in conjunction with MS/MS, which allows the determination of contaminant residues at sub-picomole level [11,12].

Capillary electrophoresis with MS detection after ionization by inductively coupled plasma (CE-ICP-MS) or UV-detection (CEUV) has also been used [13,5] although less frequently. Chen et al. [14] developed a capillary electrophoresis–electrochemiluminescence detection system, equipped with an electrically heated $Ru(bpy)_3^{2+}$/multi-wallcarbon-nanotube paste electrode. The heated electrode provided some advantages over the conventional electrode at room temperature, such as higher sensitivity, lower RSD and decreasing width of the peak. In fact, the limit of detection (S/N) ranged from 230 to 80 μg L^{-1} when the temperature increased from 22 to 49 °C.

Other non-separative methods based on polarography [15], voltammetry [16] or amperometry [17] have also been developed.

The only chemiluminescent strategy developed for dimethoate determination, was based on the reaction between ozone and the nitric oxide produced by pyrolysis at 1050 °C of dimethoate and other N-compounds, performed in the effluent of a supercritical-fluid chromatography equipment [18]. The calibration graph was linear over the range 2.96–850 mg L^{-1} of nitrogen and the detection limit was 60 pg.

On the other hand, a flow injection (FI) procedure was used coupled with a combination of ESI-MS/MS (FI-ESI-MS/MS) for dimethoate determination by John et al. [8], which allowed to

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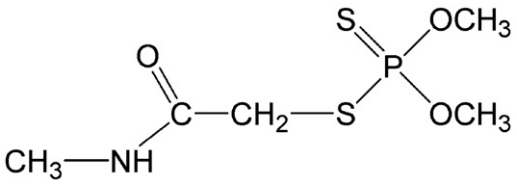

Fig. 1. Molecular structure of dimethoate.

increase the throughput. The extensive sample dilution required in that method (it was applied to plasma and urine) diluted also the matrix and consequently its potential interfering effect. Hence, similar validation characteristics as those provided by the chromatographic method (LC–ESI-MS/MS) were achieved.

In this paper FI analysis, which provides high throughput and reproducibility, has been coupled with the detection of the chemiluminescence (CL) generated by strong oxidants, in order to obtain a highly sensitive and selective method. The use of the UV light, as a derivatization tool to obtain photoproducts with better chemiluminescent properties, was also studied. However, despite the fact that photoinduced chemiluminescence (PICL) often improves sensitivity and selectivity [19], the best results were achieved in this case from the CL generated by the hydrolysis products obtained in the absence of irradiation, and the signal was greatly increased by hexadecylpyridinium chloride (HPC).

2. Materials and methods

2.1. Reagents

All solutions were prepared from analytical-grade reagents in Milli-Q water (18 MΩ-cm) from Millipore, Bedford, MA, USA, provided with a fiber filter of 0.22 μm pore-size. Dimethoate was purchased from Fluka (99.4% purity). Other reagents were: $Ce(NH_4)_2(NO_3)_6$, from Panreac; HCl and NaOH from Scharlau; CH_3COOH from J.T. Baker; and hexadecylpyridinium chloride monohydrate from Sigma. Other pesticides used were: amitrole, metazachlor, metalaxyl, thiacloprid and cyromazine (99.9%), 2,4-D and pirimicarb (99.6%), diquat monohydrate (99.4%), glyphosate and quinmerac (99.2%), fenamiphos (97.7%), diuron (99.5%), imazalil (99.8%), MCPA (98.7%), malathion (97.3%), omethoate (98.5%) and methidathion (96%), all of them from Riedel-de Haën; methomyl (99.5%) from Chem Service; Chlorpyrifos from Sigma–Aldrich (99.9%); and, diphenamide (99.9%) from Fluka.

2.2. Flow injection procedure

The FIA manifolds optimized for the CL and PICL determination of dimethoate are depicted in Fig. 2. Connections between the different parts of the flow assemblies were carried out with PTFE coil of 0.8 mm i.d. from Omnifit. Gilson (Worthington, OH, USA) Minipuls 2 peristaltic pumps, provided with tygon pump tubes from Restec, were used for flow control. The laboratory-made photoreactor included PTFE tubing (0.8 mm i.d. × 400 cm) tightly coiled around a 15 W low-pressure mercury lamp (Sylvania) for germicidal use. A 6-port medium pressure (Upchurch Scientific, Model V-450) injection valve was used. The photodetector package P30CWAD5F-29 Type 9125 photomultiplier tube (PMT) was supplied by Electron Tubes operating at 1280 V and located in a laboratory-made light-tight box. The solutions merged in a T-piece placed inside close to the flow-cell, a flat-spiral glass tube of 1 mm i.d. and 3 cm total diameter. The output was fed to a computer equipped with the CT2 counter-timer board, also supplied by Electron Tubes.

2.3. Sample preparation

Water samples from different origins, namely: irrigation, ground, spring, mineral and tap waters were tested. They were collected in plastic flaks at 4 °C and analysed before 48 h. In order to remove sand and other suspended solid matters, the samples were pretreated by filtering over a 0.45 μm membrane filter (Sartorius, Goettongen, Germany). Spiking was done by adding a proper amount of 100 mg L^{-1} of dimethoate stock solution to 50 mL of sample, in order to obtain 0.2, 0.5 and 1.0 μg L^{-1} of pesticide. Three replicates of each concentration were prepared.

A solid phase extraction (SPE) of the 50 mL of spiked samples at a flow-rate of 2–3 mL min^{-1} was performed off-line using a vacuum system and cartridges Bond Elut-C_{18}, 200 mg, from Varian, in order to improve the selectivity and sensitivity of the method. 3.0 mL of methanol, 3.0 mL of acetonitrile, 3.0 mL of methanol and 9.0 mL of water, were used to precondition the cartridges. Once the samples have been passed, the washing was performed with 9 mL of water and, next, air was passed 20 min for drying. Dimethoate was eluted by means of gravity with 1.0 mL of acetonitrile and finally under vacuum. Then 1 mL of water was passed through the cartridge to recover the remainder. Both volumes were collected in a volumetric flask of 10 mL and filling up with deionised water.

3. Results and discussion

3.1. Preliminary studies

Molecular irradiation can led to the formation of minor fragments with smaller molecular weight (fotolysis) or to induce reactions of photocyclization, photoisomerization, photooxidation and photoreduction [19]. Hence, light has been used often as a "reactive" to induce the formation of photoproducts with improved analytical properties.

A FIA manifold on the basic lines of that shown in Fig. 2b was employed for testing the influence of the irradiation on the CL

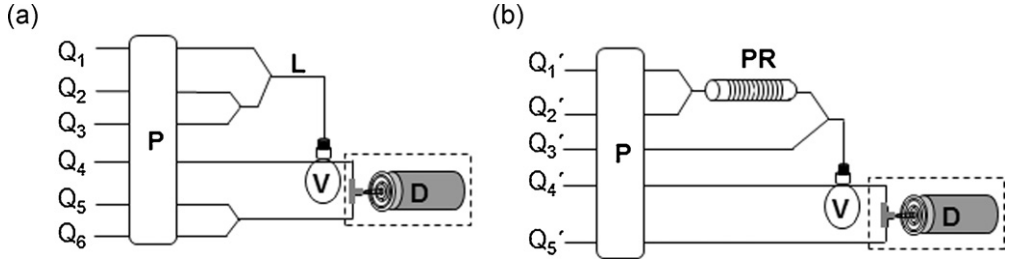

Fig. 2. Manifold configurations for dimethoate determination: (a) CL system: Q_1, dimethoate (1.6 mL min^{-1}); Q_2, NaOH 0.34 M (0.8 mL min^{-1}); Q_3, hexadecylpyridinium chloride 0.4% (0.8 mL min^{-1}); Q_4, water (14.3 mL min^{-1}); Q_5, Ce(IV) 1.8×10^{-3} M (2.2 mL min^{-1}); Q_6, HCl 2.2 M (2.2 mL min^{-1}); V, 659 μL; L, 4.5 m; hydrolysis time: 42 s. (b) PICL system: Q'_1, dimethoate (2.1 mL min^{-1}); Q'_2, NaOH 2.0 M (0.5 mL min^{-1}); Q'_3, hexadecylpyridinium chloride 0.36% (0.5 mL min^{-1}); Q'_4, water (12.2 mL min^{-1}); Q'_5, Ce(IV) 1.15×10^{-3} M in acetic acid 2.5 M (4.2 mL min^{-1}); V, 809 μL; irradiation time, 46 s. P, peristaltic pump; PR, photoreactor; V, injection valve; D, luminometer; L, PTFE tubing of 0.8 mm i.d.