Tandem chemiluminescence – flow injection analysis for dimethoate determination

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Introduction

Dimethoate (O,Odimethyl S-methylcarbamoylmethyl phosphorodithioate) is an insecticide and acaricide that exhibits both contact and systemic activity. In spite of the fact that separative methods are generally preferred in the pesticide analysis, the low cost and simplicity provided by flow injection analysis (FIA) makes this methodology an interesting alternative. The tandem with chemiluminescent (CL) detection allows to achieve the sensitivity required for analysis at trace levels.

The only CL method previously developed for dimethoate analysis, is based on reaction between ozone and the nitric oxide produced by the pyrolysis, performed in the effluent of a supercritical-fluid chromatography equipment[1].

The FIA method proposed is based on the direct CL generated by reaction with Ce(IV) in acid medium and greatly sensitized by hexadecylpyridinium chloride. The effect of irradiation with UV light on CL dimethoate response was investigated, and both, CL and photoinduced chemiluminescence (PICL) detection, were compared.

Experimental

Material and methods

A homemade luminometer provided with a P30CWAD5 type 9125B photomultiplier (Electron Tubes) was used for CL measurements and a Gilson minipuls peristaltic pump and a rotary valve (Model 161T031, NResearch) for the flow injection manifold. The photoreactor consisted of a PTFE tube helically coiled around a 15 W low-pressure mercury lamp (Sylvania).

Optimization

The preliminary experiments deal with the CL and PICL behaviour of dimethoate. The suitable oxidant was established by testing several strong oxidant systems. The best outputs were obtained

with MnO_4^-, Ce(IV) and N-bromosuccinimide and the signals were 40, 117 and 35 % higher, respectively, when sample was previously irradiated. Next steps were performed simultaneously with and without previous irradiation, and chemical and hydrodynamic parameters were studied. The configuration for CL and PICL determinations are depicted in figure 1.
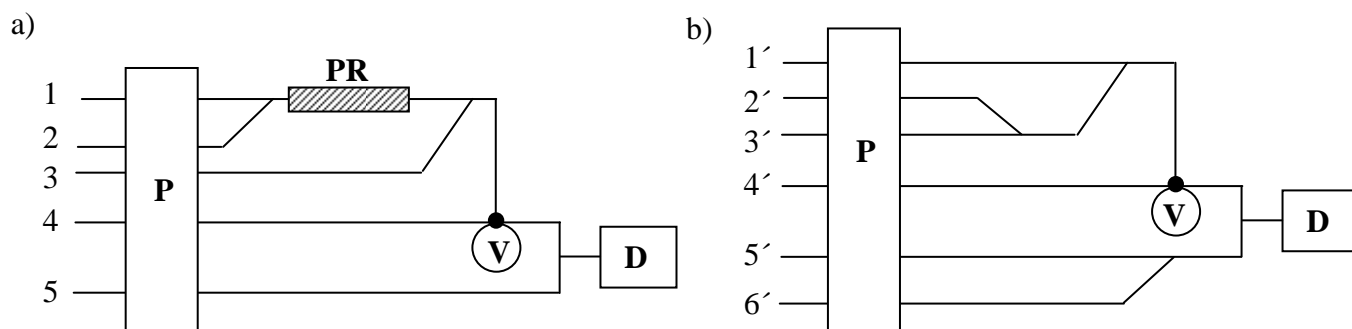
a)

b)

Figure 1. Manifold configurations for dimethoate determination:
a) <u>PICL manifold;</u> Channel 1: sample at 2.1 mL min^{-1}; Channel 2: 2.0 M NaOH at 0.5 mL min^{-1}; Channel 3: 0.36% hexadecylpyridinium chloride at 0.5 mL min^{-1}; Channel 4: water at 12.2 mL min^{-1}; Channel 5: 1.15 10^{-3} M $Ce(NH_4)_2(NO_3)_6$ in 2.5 M acetic acid at 4.2 mL min^{-1}.
b) <u>CL manifold:</u> Channel 1´: sample at 1.6 mL min^{-1}; Channel 2´: 0.34 M NaOH at 0.8 mL min^{-1}; Channel 3´: 0.4% hexadecylpyridinium chloride at 0.8 mL min^{-1}; Channel 4´: water at 14.3 mL min^{-1}; Channel 5´: 1.8 10^{-3} M $Ce(NH_4)_2(NO_3)_6$ in water at 2.2 mL min^{-1}: Channel 6´: 2.2 M HCl at 2.2 mL min^{-1}.
P: peristaltic pump; PR: Photoreactor; V: injection valve; D: luminometer.

Results

Analytical figures of merit were established for both, CL and PICL, systems (Table 1). In spite of PICL improves usually sensitivity and selectivity[2], the best results were obtained from the native CL of dimethoate, which is greatly increased by hexadecylpyridinium chloride, achieving a detection limit of 0.05 ng mL.

	CL	PICL
Intensity (I, kHz) *vs* **Concentration Relation** (C, µg mL^{-1}) (Dynamic range)	$I = 0.269 \cdot C - 0.20$ (0.5-100 µg·L^{-1})	$\log I = 1.70 \cdot \log C + 4.49$ (0.05-1 µg·mL^{-1})
LOD (S/N=3)	0.05 ng·mL^{-1}	10 ng·mL^{-1}
Inter-day reproducibility (n=5)	4.5 %	1.2 %
Intra-day repeatability (n=21)	2.8 % (0.01 µg mL^{-1})	3.8 % (0.2 µg mL^{-1})
Sample throughput	86 h^{-1}	86 h^{-1}

Table 1. Analytical figures of merit for CL and PICL methods.

References

[1] H. Shi, J.T.B. Strode, L.T. Taylor, E.M. Fujinari. *J. Chromatogr. A.* 1996; 734(2), 303.

[2] M. Catalá-Icardo, J.Martínez-Calatayud. *Crit. Rev. Anal. Chem.* 2008; 38(2), 118.