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Photo-induced chemiluminometric determination of Karbutilate in a continuous-flow Multicommutation assembly

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Abstract

The present paper deals with the chemiluminescent determination of the herbicide Karbutilate on the basis of its previous photodegradation by using a low-pressure Hg lamp as UV source in a continuous-flow Multicommutation assembly (a solenoid valves set). The pesticide solution was segmented by a solenoid valve and sequentially alternated with segments of the 0.001 $\text{mol}\,\text{l}^{-1}$ of NaOH solution, the suitable media for the formation of photo-fragments; then it passes through the photo-reactor and was lead to the flow-cell after being divided in small segments which were sequentially alternated with the oxidizing system; 2×10^{-5} $\text{mol}\,\text{l}^{-1}$ of potassium permanganate in 0.2% pyrophosphoric acid. The studied calibration range, from 0.1 $\mu\text{g}\,\text{l}^{-1}$ to 65 $\text{mg}\,\text{l}^{-1}$, resulted in a linear behaviour over the range 20 $\mu\text{g}\,\text{l}^{-1}$–20 $\text{mg}\,\text{l}^{-1}$ and fitting the linear equation: $I = (1180 \pm 30)C + (15 \pm 5)$ with the correlation coefficient 0.9998. The limit of detection was 10 $\mu\text{g}\,\text{l}^{-1}$ and the sample throughput 17 h^{-1}. After testing the influence of a large series of potential interfering species, the method was applied to water and human urine samples.

Keywords: Chemiluminescence; Photodegradation; Pesticides; Environmental samples; Multicommutation; Karbutilate; Continuous-flow

1. Introduction

Karbutilate or 1,1 dimethyl-3-(3-*N tert*-butylcarbamyloxy)-phenyl urea [1] whose molecular structure is depicted in Fig. 1 is a member of the carbamate pesticides family. This family is a large group of substituted ureas which can be represented by the molecular structure R_1–N–$RCOOR_2$ [2]; this general formula leads to three different kinds of carbamates, namely (1) derived from esters mainly used as insecticides and nematocides in which R_1 is a methyl group; (2) the herbicides (inhibiting the seed growth) presenting R_1 as an aromatic group; (3) the fungicide carbamate group with a benzimidazole group in R_1.

It has been classified as slightly in the section of acute poisoning and no carcinogenic information is provided [3]. In humans, it can produce throat pain, nauseas and vomits, diarrhoeas, consciousness troubles and convulsions and irritation on skin and eyes.

Some few papers were found in the analytical literature dealing with the Karbutilate determination; one of them is a Technical Report [4] in which several pesticides were extracted from a water solution through a solid-phase extraction column and eluted with methanol/acetone (ratio 3/2); then the note recommended to use HPLC or GC. A paper dealing with the Karbutilate determination extracted different carbamic herbicides with methanol and the filtered resulting solution was analysed with the aid of HPLC at 40 °C by using acetonitrile as mobile phase and UV–vis detection [5]. The determination of Karbutilate residues on water, soil and grass matrices was also performed with the aid of HPLC methodology [6] with photometric detection at 254 nm; the method tested the separation of mixtures of Karbutilate and some of its degradation products (from hydrolysis and demethylation processes); a previous extraction with the water–methanol mixture was also required for solid samples, and according to authors the CG determination was not possible due to the thermal instability of Karbutilate. Some papers are dealing with the separation and determination of carbamate

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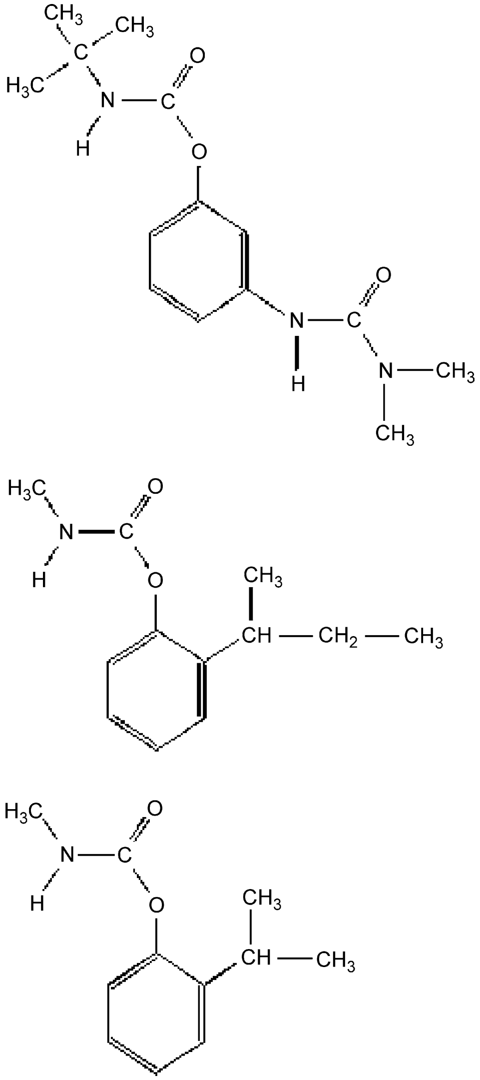

Fig. 1. Molecular structures of Karbutilate, Fenobucarb and Isoprocarb.

pesticides by liquid chromatography; one of them proposed the mass spectrometry as post-column detector for separation and detection of carbamate pesticides [7], and a summarized study of the fluid-chromatography parameters on the same group pesticides has been also published [8]. Two papers are dealing on the determination of pesticide residues in environmental samples by liquid chromatography [8] or reducing the study to the urea pesticide group [9]. A review paper dealing with the determination of urea pesticide residues can be found in literature [10].

Our general aim is to develop automated and very sensitive methods for either the determination of pesticides in water and urine samples and to be used in a post-column format when a previous separation is absolutely required. A continuous-flow assembly is prepared into the emergent Multicommutation continuous-flow methodology [11,12]; the flow assemblies of this methodology are based on a solenoid valves set for the insertion of microvolumes of sample and reagents. Detection was based on chemiluminescence measurements of the photo-products obtained upon irradiation with UV light and oxidation with a strong oxidant reagent. A systematic work on the photo-induced chemiluminescence behaviour [13] revealed a non-homogeneous behaviour of the members of the same group [14,15]; the photo-induced chemiluminescence of pesticides is strongly dependent of the chemical structure, structurally related compounds presenting scarce differences in their structure show very often different chemiluminometric behaviour. Due to that, the Karbutilate was selected for a new study. To the authors' knowledge, this is the first chemiluminescence-based determination of Karbutilate and also the first based on Multicommutation analysis.

2. Experimental

2.1. Reagents and apparatus

All reagents used were analytically pure unless stated otherwise. Solutions were prepared in purified water by reverse osmosis and then deionised (18 MΩ cm) with a Sybron/Barnstead Nanopure II water purification system provided with a fiber filter of 0.2 μm pore-size. The Karbutilate powder was from Dr. Ehrenstorfer (97.0% purity). Other used pesticides tested were Fenobucarb (99.5%) and Isoprocarb (98.3%) obtained from the same manufacturer. Chemicals such as strong inorganic acids and alkalis, buffers, oxidants as $KMnO_4$, $Ce(NH_4)_2(NO_3)_6$, H_2O_2, tensoactives and sensitizers (Triton X-100, *N*,*N*-dimethylformamide and $Na_2B_4O_7{\cdot}10H_2O$) were from Panreac, Spain; β-cyclodextrine (Fluka, Buchs, Switzerland) NH_3, Na_2HPO_4, NH_4Cl, $FeSO_4$, $FeNO_3{\cdot}9H_2O$ and sodium acetate from Probus; H_2O_2, ethanol and acetonitrile from Prolabo and Merck; KH_2PO_4, NaOH, HCl and acetic acid from J.T. Baker; sodium dodecyl sulphate and hexadecylpiridinium chloride from Fluka.

2.1.1. Preparation of the Karbutilate solution

An aqueous stock solution of 50 mg l^{-1} of Karbutilate was prepared by exactly weighing and dissolving it in purified water in an ultrasonic bath. The stock solution was protected against room light and stored into the refrigerator. The working standard solutions were daily prepared by rigorous dilution of the stock solution and also kept away from room light.

Preliminary experiments were aimed to check the kinetic stability of aqueous stock solutions of the herbicide Karbutilate; the solutions containing 50 mg l^{-1} of Karbutilate were protected from room light and kept at 4 °C into the refrigerator. UV–vis spectra were periodically recorded, from 200 to 500 nm up to 8 days. No relevant variations on the absorbance spectra were observed.

2.1.2. Flow assembly

The continuous-flow manifold is depicted in Fig. 2 and it consisted of a PTFE coil of 0.8 mm i.d.; a Gilson (Worthington, OH, USA) Minipuls 2 peristaltic pump provided with pump tubing from Elkay Elreann (Galway, CO, USA); three Model 161T031 solenoid valves (NResearch, Northboro, MA, USA). The photo-reactor consisted of a 150 cm length and 0.8 mm i.d. PTFE tubing helically coiled around a 15 W low-pressure