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

C.M.P.G. Amorim [a,1], J.R. Albert-García [a], M.C.B.S. Montenegro [b], A.N. Araújo [b], J. Martínez Calatayud [a,*]

[a] *Department of Analytical Chemistry, University of Valencia, Valencia, Spain*
[b] *REQUIMTE, Departamento de Química Física, Faculdade de Farmácia (UP), Portugal*

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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 mol 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} mol l^{-1} of potassium permanganate in 0.2% pyrophosphoric acid. The studied calibration range, from 0.1 μg l^{-1} to 65 mg l^{-1}, resulted in a linear behaviour over the range 20 μg l^{-1}–20 mg 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 μg 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.
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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

* Corresponding author. Tel.: +34 96 354 4062; fax: +34 96 354 4062.
E-mail address: jose.martinez@uv.es (J.M. Calatayud).
[1] Present address: Faculdade de Farmácia, Universidade de Porto, Porto, Portugal.

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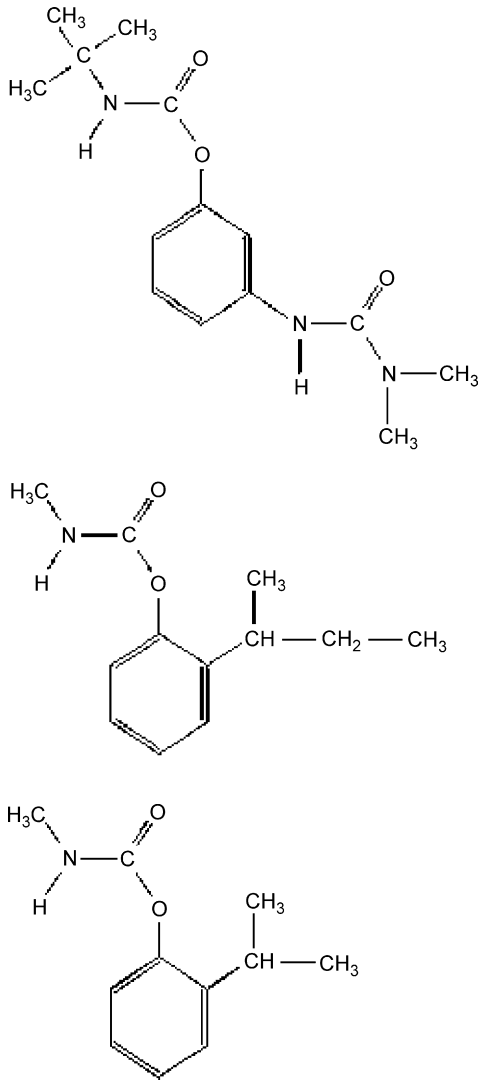

Fig. 1. Molecular structures of Karbutilate, Fenobucarb and Isoprocarb.

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 fibber 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

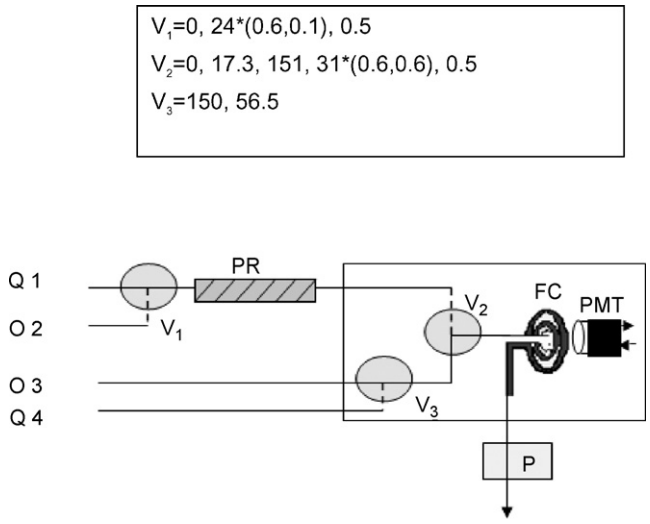

Fig. 2. Multicommutation continuous-flow assembly for the photodegradation—chemiluminescent determination of Karbutilate; Q_1, pesticide solution; Q_2, suitable medium for the UV-irradiation; Q_3, oxidant in acidic medium solution; Q_4, pure water; P, peristaltic pump; PMT, photomultiplier tube; V_1, V_2 and V_3, solenoid valves; FC, flow-cell; PR, photo-reactor. On top is the hydrodynamic parameters program for the solenoid valves.

mercury lamp (Sylvania) for germicidal use. The flow-cell was a flat-spiral quartz tube of 1 mm i.d. and 3 cm total diameter backed by aluminium foil as a mirror for maximum light collection. The photodetector package was a P30CWAD5F-29 Type 9125 photomultiplier tube (PMT) supplied by Electron Tubes operating at 1280 V; it was located in a laboratory-made light-tight box. The output was fed to a computer equipped with a counter-timer, also supplied by Electron Tubes.

The equipment was periodically tested by means of a chemiluminescent system based on the oxidation of the Aldicarb by 7×10^{-4} mol l^{-1} MnO_4^- in 2.0 mol l^{-1} H_2SO_4. The test was performed twice every day, before and after the studies with the Karbutilate and according to the procedure published elsewhere [11].

2.2. Procedures

2.2.1. Optimization of experimental parameters

The optimization of all experimental parameters was performed by a sequential combined methodology. First the chemical parameters (oxidant system, medium for photodegradation, surfactants, sensitizers and temperature combined with flow-rate) were optimized by using the unvaried method. The flow parameters (size and number of segments, flow-rate and photodegradation time interval) were optimized by using a multivariate strategy; the modified simplex method (MSM) [16–18].

Two consecutive simplex procedures were performed; the interval for each variable in the second being restricted to the zone that gave the best results in the first. Then some of the higher vertices were selected for a new and large comparative ($n = 20$) study to choose the output resulting in the best compromise sensitivity (peak height), sample throughput (peak-base width) and reproducibility.

2.2.2. Preparation of samples

Human urine and water samples of different type were collected from different places, namely tap water, surface water and commercially available bottled water. Samples were collected in plastic flaks at 4 °C. No sample pre-treatment was required, only filter when they presented a turbid appearance. All samples were spiked with the required volume of the stock solution (100 mg l^{-1} of Karbutilate) to obtain solutions containing 0.25 mg l^{-1}.

3. Results and discussion

Former preliminary studies consisted in a large screening to test the susceptibility of carbamate family pesticides to present chemiluminescent emission [10] being or not irradiated with UV light (lamp ON and lamp OFF) and irradiation time of 2 min and 30 s on solutions containing 50 mg l^{-1} of pesticide.

Different chemical media were used for the photodegradation tests, namely H_2O, as reference; H_2O_2, 0.05%; Fe(III) (monohydrate ferric nitrate) 6×10^{-5} mol l^{-1}; Fe(II) (hepta-hydrate ferrous sulphate) 6×10^{-5} mol l^{-1}; NaOH 10^{-3} mol l^{-1}. After being irradiated the resulting solutions were segmented with the solution containing 7×10^{-4} mol l^{-1} potassium permanganate in 2.0 mol l^{-1} sulphuric acid medium. Studies on Karbutilate revealed an interesting analytical procedure was possible; very small emission intensities were observed with lamp OFF; however, a clear chemiluminescent emission was observed with lamp ON. The higher outputs were observed with the NaOH medium for photodegradation.

Further preliminary assays were performed on Karbutilate and consisted in screening simultaneously the influence of different oxidant systems with different UV-irradiation media.

The suitable oxidant was established by testing some strong oxidant systems (oxidative reagent plus medium for the oxidation), namely 7×10^{-4} mol l^{-1} potassium permanganate or 6×10^{-3} mol l^{-1} Ce(IV) (both of them in 2.0 mol l^{-1} H_2SO_4); 6×10^{-3} mol l^{-1} $Fe(CN)_6^{3-}$ in 1.5 mol l^{-1} NaOH; the higher outputs were obtained with the systems (medium for photodegradation-oxidant) NaOH-$KMnO_4$ and H_2O_2-$Fe(CN)_6^{3-}$. Two different systems resulted in higher outputs, namely (a) potassium permanganate in pyrophosphoric acid medium (other mineral acids were tested too) with photodegradation in NaOH 0.001 mol l^{-1}; (b) hexacyanoferrate (III) in alkaline medium with the photodegradation in basic medium and 0.05% of hydrogen peroxide. Results are depicted in Fig. 3.

A further experiment was performed to select the suitable system by testing different concentrations of Karbutilate over the range 5–50 mg l^{-1} with both pre-selected photodegradation media (hydrogen peroxide and NaOH). The highest outputs and smaller blank outputs were obtained with the system NaOH medium for photodegradation and as oxidant, potassium permanganate in pyrophosphoric acid medium.

3.1. Optimization of the oxidation system parameters

The influence of potassium permanganate concentration was tested over the interval 10^{-6}–10^{-2} mol l^{-1} and with 10 mg l^{-1}

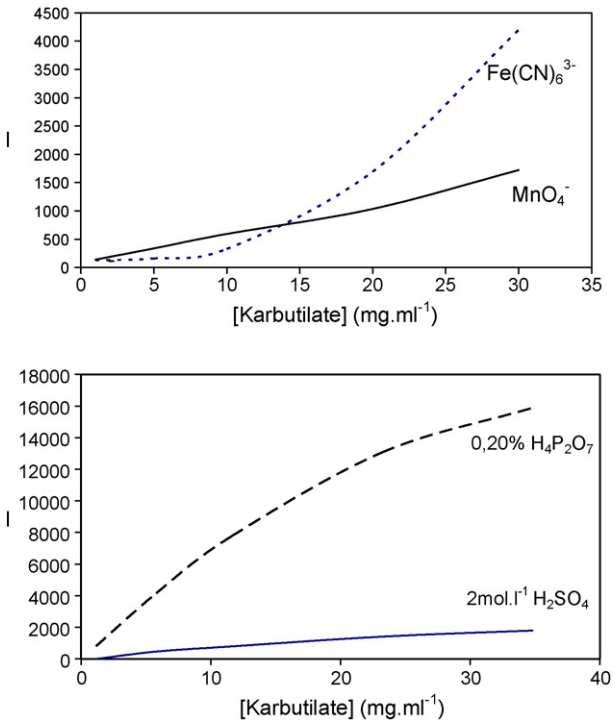

Fig. 3. Influence of the two pre-selected oxidant systems concentrations (on top) and influence of the sulphuric and pyrophosphoric acid as oxidation media.

of the herbicide. As observed in formerly published articles [19–21] this parameter resulted to be critical with a short maximum interval close to 2×10^{-4} mol l^{-1}. Results are depicted in Fig. 4a. This concentration of potassium permanganate was tested with different concentrations of pyrophosphoric acid over the range 0.05–0.50%; when concentration was increased up to 0.1%, the height of the outputs increased abruptly following a mild increase up to around 0.2% and being a plateau for the remaining tested range. Selected for further work was 0.2% (see Fig. 4b).

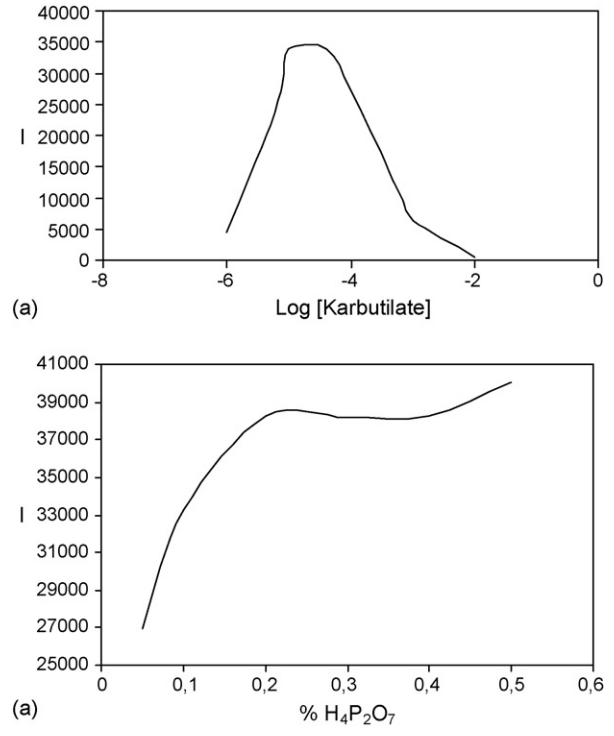

Fig. 4. Optimization of chemical parameters: (a) influence of oxidant concentration; (b) influence of the pyrophosphoric acid concentration.

3.2. Influence of organized media and sensitizers

The presence of two different kinds of chemicals, organized media (some tensoactives and β-cyclodextrine) and sensitizers was tested. Tensoactive solutions were prepared in concentrations over the critical micellar concentration (c.m.c.); chemicals and concentrations tested were: β-cyclodextrine 0.73%; benzalkonium chloride 0.54%; *N*-cethyl-*N*,*N*,*N*-trimethylammonium bromide 0.11%; hexadecylpiridinium chloride 0.11%); sodium dodecylsulphate (SDS) 0.68%; Triton X-100 0.064%. No increased emission was obtained higher than the observed with pure Karbutilate solution. Similar experiments were performed to check the behaviour of sensitizers. Tested compounds and concentrations were: 2-propanol 20%; acetonitrile 20%; dimethylformamide 5%; ethanol 5%; formic acid 0.5% and quinine sulphate 10^{-4} mol l^{-1}. Results are shown in Fig. 5.

Relevant increases of the output were observed only with the presence of propanol; however, its use was refused due to the high blank emission which leaded to results without the required reproducibility.

3.3. Combined influence of the temperature with the variation of the flow-rate

The influence of temperature presents different effects (complex effects) on these systems [15,22] either on the photodegradation or on the chemiluminescent process. The basic consideration on chemiluminescence is temperature rise can decrease the emission intensity through an increased probability of deactivation via external conversions; on the other hand, chemiluminescent reaction can be affected by temperature in both thermodynamic and kinetic terms. Due to these kinetics effects the influence of temperature on the height of the outputs could be closely related to the flow-rate (maximum light could be emitted when the sample plug passes the front of the PMT window). On the other hand, the influence of temperature resulted in low reproducibility when its influence was achieved by immersing the flasks containing solutions into the water bath; it was probably due to small and continuous diminution of the oxidant concentration at high temperature (internal redox process due to the presence of small impurity amounts). The experiment was performed by immersing into the bath about 180 cm of PTFE coil flowing the oxidant solution and testing the influence of a given temperature at different flow-rates (measured at the outlet of the manifold). Higher outputs were observed at any tested flow-rate over the range 55–60 °C; selected for further work were 10 ml min^{-1} and 60 °C. All the following work was performed at 60 °C with immersed 180 cm of the coil in the way reservoir-valve 3.

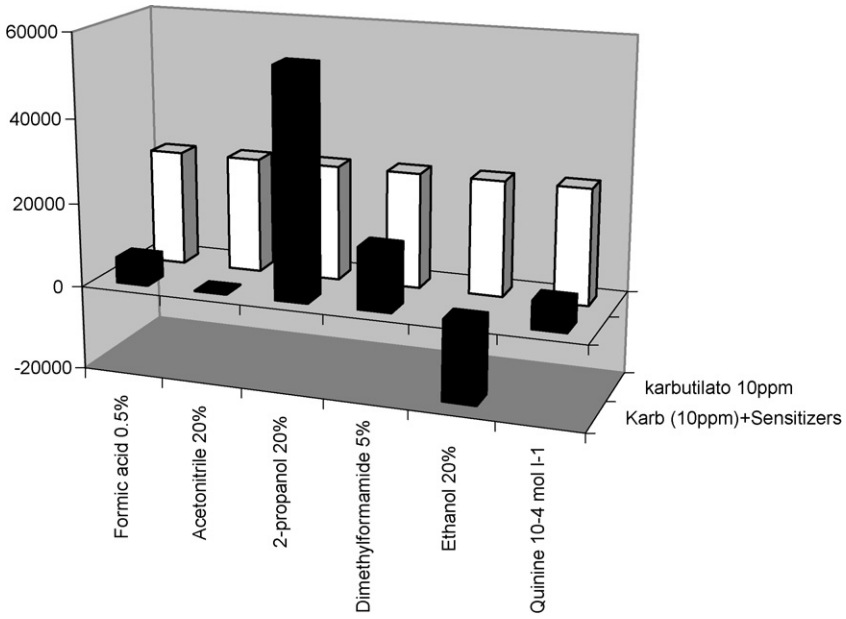

Fig. 5. Influence of the sensitizers presence on the emission outputs.

3.4. Optimization of hydrodynamic parameters

A multiparametric strategy, the modified simplex method, was selected for the optimization of hydrodynamic parameters. The parameters included the number and volume of inserted segments (sample, media and oxidant) through valves 1 and 2; global flow-rate (Q_1 and Q'_1 were kept at same flow-rate) and time for the photodegradation. Fig. 2 shows the resulting solenoid valves program with the values (in seconds) selected as optimal conditions.

The irradiation time is a relevant parameter and it is determined by the flow-rate of sample and photodegradation medium and the length of the reactor tubing; or, alternatively by controlling the stopped-flow interval [23].

3.4.1. Photodegradation of Karbutilate (carbamates)

Photochemical studies have aroused much interest as a clean, cheap and reproducible analytical tool in different fields. Up to the author's knowledge, there is no information about the nature of the photoproducts obtained after the irradiation with UV light of a aqueous solution of Karbutilate.

The life-span of pesticides and the required conditions for the sunlight-based photo catalytic photodegradation processes have been described in a certain number of environmental studies; even this photodegradation has been proposed as a straightforward, affordable and cost-effective method for the in situ control of environmental pollutants [24]. Mainly differences on environmental studies and those based on analytical purposes are based on the environmental results. The sunlight is one of the agents acting on the metabolic degradation so it should be added water, soils bacteria, enzymes; and a certain number of actions from plants and animals. As example it can be reported studies on chloroprophan leaded to a chloroanalines as the final degradation products [25]. Studies dealing on the irradiation of some herbicides when sprayed on soil and foliage leaded to conclude the degradation of *N*-methyl carbamates (Fenobucarb and Isoprocarb among others were studied) was not only due to the sunlight irradiation (similar results were obtained by means of an UV (λ 254 nm) lamp. Some authors [26] established a procedure based on irradiation followed by an enzymatic attack and according to other sources first step in the degradation of carbamates is soil hydrolysis [27]; simple esters to the parent unstable acid and alcohol [28]; or to their respective anilines. In alkaline soil (like the irradiation of Karbutilate in the present paper) the carbamate Phenmedipharm was converted hydrolytically to methyl-3-hydrophenyl-carbamate which then was hydrolysed to 3-aminophenol.

Reported experiments dealing on carbamates solved in aqueous solutions and exposed to photo-decomposition under the effects of artificial ultraviolet radiation, concluded the pH of the medium was an important factor in relationship to the rates of photolysis which were slow at low pH values and increased with increasing pH value. These results are in accordance with the experimental results obtained in this study by selecting the alkaline solution (with potassium permanganate and hexacyanoferrate(III)) as the suitable medium to irradiate the Karbutilate. The primary effect of the UV-irradiation appears to be cleavage of the ester bond resulting in the production of the phenol or heterocyclic enol of the carbamate esters tested. The hydrolysis products produced were further photo-decomposed to other unidentified degradation products. As example Carbaryl produced five degradation products, one of which was identified as 1-naphthol. It is assumed that, apart from the cleavage of the ester bond, changes at other positions in the molecule are produced by irradiation; however, the intact carbamate ester group is retained. The light absorption characteristics of the carbamate pesticides influenced the extent of the decomposition by a specific light source and being very influential the presence of solvents [29–31]

To assess the molecular structure changes on the irradiation step, the UV–vis and fluorimetric spectra of Karbutilate both, with lamp ON and OFF and in the NaOH medium, were obtained. A simple flow assembly consisting in two merging channels with the aid of a PTFE "T" piece nesting close to the photo-reactor was used; an aqueous solution containing 10 mg l^{-1} of Karbutilate flowed through one channel and the NaOH solution for the photodegradation medium flowed through the second and the flow-rate was adjusted to reproduce the same irradiation interval.

The fluorescence intensity was null with lamp OFF and negligible with irradiation. The UV–vis spectral profiles are very similar which means the irradiation did not affect the part of the molecular structure mainly responsible for the absorption (the aromatic ring).

4. Analytical figures of merit

The dynamic range was comprised between 0.1 μg l^{-1} and 65 mg l^{-1} of Karbutilate, the linear behaviour was observed over the range 0.01–20 mg l^{-1}, fitting with the average equation (five independent calibrations performed with freshly prepared solutions in five different days) $I = (1180 \pm 30)C + (15 \pm 5)$ with a correlation coefficient of 0.9998 ($n = 5$).

The limit of detection was 10 μg l^{-1} and it was defined as three times the blank output height average and was empirically established by decreasing the concentration of injected Karbutilate until this relationship was reached. The reagent consumption was 0.24 ml by sample insertion.

The repeatability (R.S.D. in %), for a series of five injections of 0.1 mg l^{-1} of Karbutilate, was 3.3%, and the throughput empirically determined from the same series was 17 h^{-1}.

The robustness of the analytical procedure to chemical parameters (potassium permanganate and pyrophosphoric acid concentrations), or perseverance of signal when the experimental parameters are altered, was studied in a range over ±20% around the optimal conditions. Relative errors were calculated by comparison with the outputs from the reference (optimal conditions). Variations of potassium permanganate concentrations up to ±5% did not result in relevant relative errors (under 5%); however, these variations on the acidic concentrations resulted in very high relative errors, over 10%.

The study of the potential interfering species was performed by adding different amounts of these substances to a 0.6 mg l^{-1} Karbutilate solution and comparing the analytical outputs with the reference (pure Karbutilate solution); maximum tested concentrations 500 mg l^{-1}. More serious interferences were observed with nitrite, nitrate, carbonate, Mn(II) and Fe(II). Nitrite, Fe(II) and carbonate were tested again at 500 mg l^{-1} but solutions were boiled previously to the chemiluminescence emission, for less than 5 min; no interferences were observed. To eliminate interferences from Mn(II) and nitrate, both at 500 mg l^{-1}, the sample solutions were forced through a column containing an ion-exchanger resin; Duolite C_{20} anionic (from Probus) to eliminate nitrate and Duolite A-102D (also from Probus) cationic to separated Mn(II); both interferences disappeared (see Table 1).

Several water samples were collected from different places and were spiked with a known amount of the pesticide (0.25 mg l^{-1}). Human urine samples were also investigated by spiking the pesticide at the same concentration. Collecting place and obtained recoveries (as %) and R.S.D. were as follows: tap water (Burjassot, Valencia, Spain) 100.6, 0.6; surface waters (Ontinyent, Valencia, Spain) 101.7, 0.7; bottled mineral water (trade mark Agua de Bejis, Castellón, Spain), 102.3, 0.6. The urine samples presented a intense chemiluminescent emission previous to be spiked with the pesticide (0.25 mg l^{-1}) and, due to it, different kinds of solid–liquid extraction cartridge was tested to obtain a complete separation of the pesticide from the rest of the sample. Cartridge Bond Elut C18 from Varian and elution with 10% acetonitrile elution resulted to be a suitable procedure. Recoveries and R.S.D. (both as %) with five replicates were: sample 1 (male) 99.8, 04; sample 2 (female) 100.9, 1.1; sample 3 (male) 99.4, 2.5.

Finally and to test the general applicability of the method (post-column format), the optimized flow-system was applied

Table 1
Influence of potential interferents

Tested interferents (cations)	C (mg l^{-1})	Error (%)	Tested interferents (anions)	C (mg l^{-1})	Error (%)
Fe^{3+}	50	−3.4	HCO_3^-	250	−4.1
Fe^{2+}	5	−3.4	CO_3^{2-}	5	2.1
Ca^{2+}	50	−4.1	Cl^-	500*	5.0
NH_4^+	50	−3.9	CrO_4^{2-}	500*	4.0
Mn^{2+}	1	−2.6	CN^-	500*	−0.1
K^+	500*	−3.5	SO_4^{2-}	500*	0.1
Na^+	500*	3.7	NO_2^-	0.2	0.1
Cu^{2+}	100	0.6	NO_3^-	50	2.7
Cr^{3+}	500*	3.6	CH_3COO^-	500*	5.0
Zn^{2+}	250	−1.8	$H_2PO_4^-$	5	−1.0
Mg^{2+}	100	−4.9			
Co^{2+}	25	4.3			
Pb^{2+}	50	−2.5			
Ni^{2+}	25	−5.0			
Urea	500*	4.7			

* Maximum assayed concentration with 0.6 mg l^{-1} of Karbutilate.

Table 2
Analytical figures of merit for two members of the Karbutilate family

	Isoprocarb	Fenobucarb
L.O.D. ($\mu g\,l^{-1}$) (3σ)	30	50
R.S.D. intraday ($n=17$) (%)	4.6	2.6
Recovered surface water (%)	102.4 ± 1.7	103.1 ± 2.1
Recovered tap water (%)	103.6 ± 2.4	99.6 ± 2.6
Recovered bottled water (%)	101.2 ± 0.9	105.1 ± 2.4
Recovered human urine* (%)	94.7 ± 3.4	95.1 ± 2.9

* Obtained results through the standard addition procedure.

to two carbamate pesticides which as far as authors know have not been studied on these kind of procedures, Fenobucarb and Isoprocarb, whose molecular structures are represented in Fig. 1 [32,33]. Table 2 depicts the analytical figures of merit obtained for these two carbamates.

5. Conclusions

A new analytical procedure is proposed for the herbicide Karbutilate based on the photo-induced chemiluminescence of the analyte with a procedure different to other carbamate pesticides [10–12]. UV-irradiation was performed in NaOH medium and the potassium permanganate was the suitable chemiluminescent oxidant.

The procedure presents competitive analytical figures of merit and it is applied to several water and a human urine samples.

A discussion about the possible irradiation products is also included.

Finally, the use of solenoid valves allows the easy, complete automation of the process with low sample and reagent consumption.

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