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Photoinduced-Chemiluminometric Determination of Imidazolinone Pesticides in a Multi-Commutated Flow-Assembly

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Abstract

A fully automated method for determination of imidazolinone pesticides in tap and mineral waters is proposed. The automation of the flow assembly is based on the multi-commutation approach, which uses multiple solenoid actuated micro-solenoid devices strategically positioned in the flow manifold. The determination of imazapyr, imazaquin and imazamethabenz-methyl is performed on the basis of the photodegradation of pesticides by using a photoreactor consisting of 150 cm x 0.8 mm PTFE tubing helically coiled around a 20 W low-pressure mercury lamp. UV irradiation of imidazolinone pesticides (270s) turns into strong chemiluminescent photoproducts in presence of potassium permanganate as oxidant. The method is linear up to 10 mg L^{-1} for all imidazolinones; the limit of detection and reproducibility (as the RSD of 10 peaks of a 0.5 mg L^{-1} solution) are 0.05 mg L^{-1} and 1.3 % (imazapyr), 0.1 mg L^{-1} and 2.2 % (imazaquin), and 0.01 mg L^{-1} and 1.4 % (imazamethabenz-methyl). The sample frequency is 12 h^{-1}.

Keywords Imidazolinone pesticides**,** multi-commutation, chemiluminescence, photodegradation.

1. Introduction

Imidazolinones are a relatively new class of herbicides, first appearing in 1981. They are among the most popular choices for farmers worldwide, because they are nontoxic to animals and highly selective. Imidazolinone herbicides are a potent commercial herbicides family and an essential part of the multibillion-dollar weed-control market. They are more effective against broadleaf weeds than grasses, and have both foliar and soil activity. Imidazolinones kill plants by inhibiting acetohydroxyacid synthase (AHAS), which is localized in plant meristematic tissues, and are involved in the biosynthesis of branched-chain essential amino acids valine, leucine and isoleucine. This causes a disruption of protein synthesis which in turn leads to interference in DNA syntheses and cell growth [1-3].

The basic structural requirements for the imidazolinone class of herbicides consist of an aromatic ring (pyridine, quinoline or benzene), carboxylic acid or carboxyester and an adjacent *ortho*-imidazolinone ring (Figure 1).

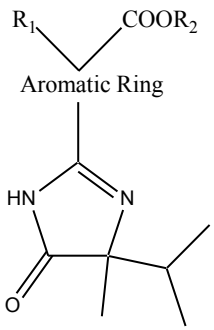

Fig. 1 Formula of imidazolinone pesticides.

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In the area of environmental analysis of imidazolinones, analytical methods including HPLC with UV [4-6] and mass spectroscopy detection [7,8], HPLC separation on polysaccharide-coated chiral phases [9], GC/MS [10], and fiber optic immunosensors [11, 12] have been employed. Due to the simplicity, low cost and high sensitivity and selectivity, chemiluminescence (CL) based detection has become in the last years a quite useful detecting tool in flowing methodologies. Nevertheless, CL-techniques for organic pesticides residue analysis have been limited by the fact that, relatively few of these compounds are strongly chemiluminescent. This can be overcome by means of different analytical strategies, namely, photochemically-induced chemiluminescence (Ph-CL) [13-16].

On the other hand, the use of multiple solenoid actuated micro-solenoid devices strategically positioned in the flow manifold (multi-commutation) has led to significant attainments mainly in relation to the improvement of analytical features of flow analysis, namely, reproducibility, reduction of sample and reagents consumption, degree of automation and versatility [17]. Despite its analytical potential, multi-commutation has been applied scarcely to the quantitative analysis of pesticides [18-22].

The immediate purpose of the present work was to develop a simpler assay for determination of imidazolinone pesticides using a fully automated multi-commutation flow system coupled to Ph-CL. Photoproducts were determined by direct chemiluminescence employing potassium permanganate as oxidant. The method has been applied to the determination of imidazolinone herbicides in tap and mineral waters. The method allows on the basis of the Ph-CL approach the determination of pesticides (as imazaquin, imazapyr and imazamethabenz-methyl) which present very weak or nulle native chemiluminescence. The proposed method could be useful e.g. for post-column detection in HPLC. To the authors' knowledge, there is no references devoted to the chemiluminometric determination of imidazolinones.

2. Experimental

2.1. Reagents

All reagents were analytically pure unless stated otherwise and prepared in deionised water (18 MΩ cm) using a Sybron/Barnstead Nanopure II water purification system. Imidazolinones (imazapyr, imazaquin and imazamethabenz-methyl) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Mineral acids and alkalis, $KMnO_4$, H_2O_2 tested in preliminary assays (all from Panreac, Barcelona, Spain). $Fe(NO_3)_3 \cdot 9H_2O$ (Probus, Barcelona, Spain) and $FeSO_4 \cdot 7H_2O$ (Fluka, Buchs, Switzerland). Acetone (from Guinama, Valencia, Spain), quinine sulphate, Rhodamine B and 6G (from Sigma-Aldrich Química S.A, Madrid, Spain), β-cyclodextrins (Fluka), formic acid, acetonitrile, 1,4-dioxane and dimethylformamide (all from Panreac), tetrahydrofuran (THF) and Triton X-100 (Scharlau, Barcelona, Spain), sodium dodecyl sulphate (SDS), hexadecylpyridinium chloride (Fluka), ethanol (Prolabo, Barcelona, Spain), respectively, were tested as photolysis and chemiluminescence enhancers. Cations tested as potential inorganic interferences were prepared from chloride (Cu(II)), and sulphate salts (Mn(II), Zn(II), Mg(II)) (all from Panreac). $KHCO_3$ and NH_4HCO_3 (Panreac). Anions from sodium salts were also from Panreac.

2.2. Apparatus

The flow manifold used (see Fig.2) comprised a PTFE coil of 0.8 mm ID and a Gilson Minipuls 2 (Worthington, OH, USA) peristaltic pump. For the fully automated manifolds three Model 161T031 solenoid valves (NResearch, Northboro, MA, USA, http://www.nresearch.com) were used. The solenoid valves were connected to a laboratory-made interface type KSP.

Its actuation was programmed using a home-made solenoid salves software running on a Pentium-type computer in Microsoft Windows 98. The programme and interface allow an independent control of the solenoid valve, the sequence of insertions and the number of cycles according to the number of samples, reagent solutions or standards to be inserted.

The photo detector package was a P30CWAD5F-59 Type 9125B photomultiplier tube (PMT) supplied by Electron Tubes operating at 1280 V (spectral range 280-630 nm) and 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 flow cell was a flat-spiral quartz tube of 1mm inner diameter and 3 cm total diameter backed by a mirror for maximum light collection.

2.3. Procedures

2.3.1. Stock solution preparation

Stock standard solutions of pesticides (ca. 50 mg L^{-1}) were prepared by exactly weighing and dissolving the pesticide in deionised water. The working standard solutions were freshly prepared by diluting the stock standard solution in the appropriate volume of deionized water. All solutions of pesticides were protected from light.

2.3.2. Analytical measurements and solenoid valve flow–assembly

The flow system designed comprised three solenoid valves, each one acting as an independent switch (see Fig.2). Two of the three valve ports are permanently connected. The peristaltic pump was placed after the detector and the sample and reagent streams were driven to the detector flow-cell by aspiration at a flow-rate of 10 mL min^{-1}.

The way of work of a valve can be described as follows: N*(t_1, t_2), where t_1 is the time of valve in ON, t_2 is the time of valve in OFF and N is the number of cycles ON/OFF. Changes in the manifold affected only the number and length of pulses (time ON/time OFF) applied to each solenoid valve. The optimised insertion profile for obtaining a typical transient analytical signal is depicted in Fig.3b).

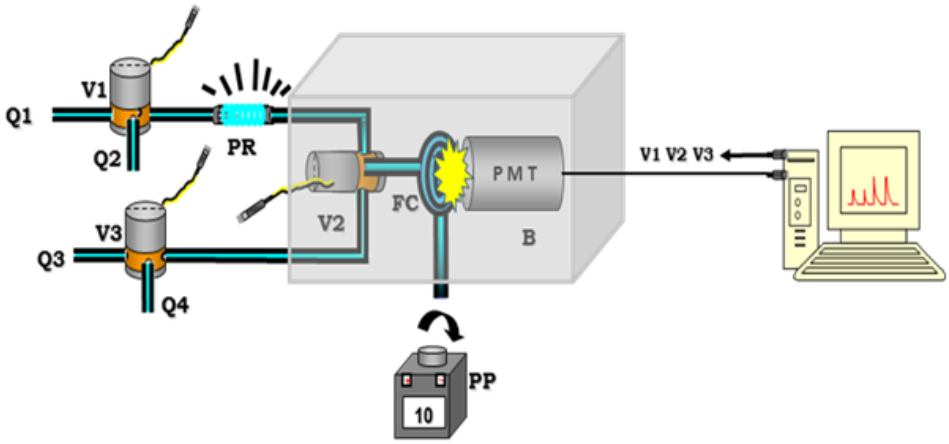


Fig. 2 Solenoid valve flow-assembly for determination of imidazolinones.
a) Preliminary tests. Q_1: pesticide aqueous solution (75 mg L^{-1}), Q_2: medium of photodegradation (a: NaOH 10^{-3} M, b: H_2O_2 0.05%, c: H_2O, d: Fe(II) 6 10^{-5} M, e: Fe(III) 6 10^{-5} M), Q_3: oxidant ($KMnO_4$ 7 10^{-4} M in H_2SO_4 2 M), Q_4: deionised water.
b) Optimised manifold. Q_1: pesticide aqueous solution, Q_2: photosensitizer: acetonitrile 5%, Q_3: oxidant ($KMnO_4$ 2 10^{-4} M in H_2SO_4 2 M), Q_4: deionized water. V1, V2 and V3: solenoid valves, PR: photoreactor, PP: peristaltic pump (flow-rate 10 mL min^{-1}), PMT: photomultiplier tube, FC: spiral flow-cell, B: light-tight box.

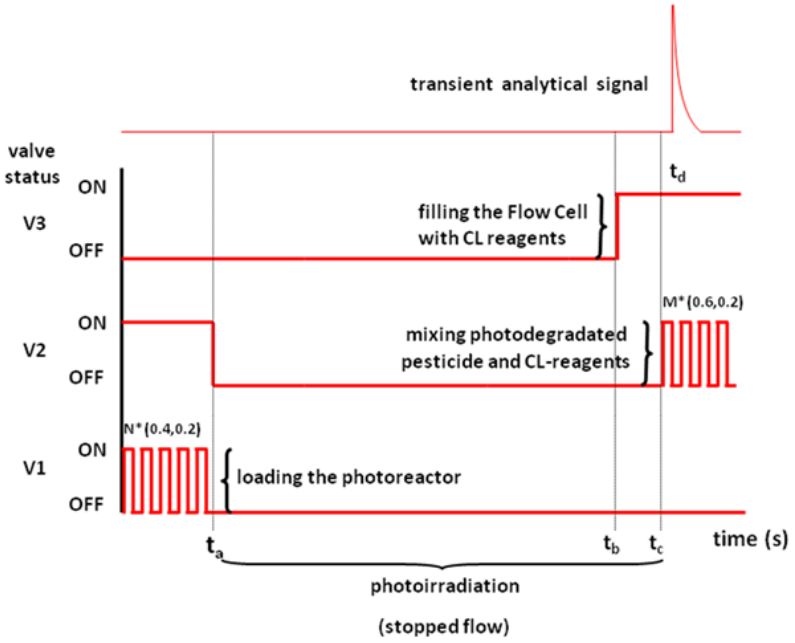


Fig. 3 Schematic profile of a multi-insertion cycle. N*(t_1, t_2). N: number of insertions. In each insertion the solenoid valve is t_1 seconds ON and t_2 seconds OFF.
a) *Preliminary tests:* N= 50, M= 32, t_a = 3 s, t_b = 165 s, t_c = 15 s, t_d = 40 s.
b) *Optimised manifold:* N= 30, M= 30, t_a = 18 s, t_b = 273 s, t_c = 19 s, t_d = 39 s.

First, 30 alternated micro insertions of pesticide and medium of photodegradation were performed. During each micro insertion V1 remains activated during 0.4 s (valve ON, imidazolinone Q_1 is aspirated), and deactivated during 0.2 s (valve OFF, medium of photodegradation Q_2 is aspirated). During the 18 s that the sample insertion takes place, V2 remains in ON, allowing that the photoreactor fills of the mixture pesticide-medium of photo degradation. This loading time also is used for washing the inner walls of the photoreactor avoiding contamination between samples. Then V1 and V2 are switched simultaneously and remain OFF during 270 s of stopped-flow (time of UV photo irradiation). Previously to the chemiluminescent reaction (t_b=273 s,), chemiluminescent reagent ($KMnO_4$ (Q_3)) is aspirated to the flow cell by switching ON/OFF valve V3. After the stopped flow, V2 is activated and 30 alternated micro segments of photodegradated pesticide and mixture of chemiluminescent reagents are inserted. A chemiliminometric response is obtained and the transient analytical signal returns to the base line ready for a new cycle.

The physical configuration of the flow system was the same for all experiments performed in the present work. The flow system was developed as a flexible manifold, in which an independent control and reconfiguration of the mono-commuting elements is possible without requiring a physical reconfiguration of the flow manifold. In fact, the optimization of the flow manifold consists in a fast and easy process *via* software, where the only variables involved are the insertion profile of solenoid valves, namely, sequence, number and duration of electronic pulses operating solenoid elements.

2.3.3. Preparation of samples

The proposed method was applied to the determination of imidazolinone pesticides in spiked tap and mineral water.
(a) *Tap water* samples from the town of Moncada in Valencia, Spain were diluted (1:5) and spiked with pesticide standard solutions to obtain solutions containing imidazolinones in the vicinity of 0.5, 3 and 5 mg L^{-1}.
(b) *Natural mineral water*. Bezoya natural mineral water is owned by Group Leche Pascual, SA and proceeds from the spring Bezoya Ortigosa del Monte in Segovia, Spain where it is also packaged. Bottled mineral water samples were spiked with pesticide standard solutions to obtain solutions containing imidazolinones in the vicinity of 0.5, 3 and 5 mg L^{-1}.

3. Results and discussion

3.1. Preliminary tests. Photodegradation of imidazolinones

First, the homogeneous-phase photodegradation of imidazolinones in different media and combined with chemiluminescence detection of the photo-irradiated herbicides was studied.

Imazapyr, imazaquin, imazamthebenz-methyl (actually a mixture of imazamethabenz A (*2-(4-Isopropyl-4-methyl-5-oxo-4,5-dihydro-1*H-*imidazol-2-yl)-5-methyl-benzoic acid methyl ester*) and imazamethabenz B (*2-(4-Isopropyl-4-methyl-5-oxo-4,5-dihydro-1*H-*imidazol-2-yl)-4-methyl-benzoic acid methyl ester*) and imazethapyr were selected between the imidazolinone family attending criteria of chemical structure variability. Imazapyr and imazethapyr present an aromatic pyridine ring whereas imazaquin and imazamethabenz-methyl exhibit a quinoline and benzene ring, respectively. Moreover, imazapyr, imazaquin and imazethapyr are carboxylic acids, presenting imazemethabenz-methyl a carboxymethyl group. In addition, imazapyr and imazaquin do not present methyl (imazamethabenz-methyl) and ethyl substituents (imazethapyr) connected to the aromatic ring (see Table 1).

The study of photodegradation media was focused on chemical species forming after UV irradiation hydroxyl radicals that react with organic pollutants in a non-selective manner and lead to an efficient photocatalyst for pesticide degradation [23]. NaOH, Fe(II) and H_2O_2 employed in the photo-Fenton reaction [24], and Fe(III) aqua complexes described as an efficient photocatalytic system for the mineralisation of pesticides by sunlight irradiation [25] were tested.

On the other hand, direct chemiluminescence uses strong oxidants ($KMnO_4$, $Fe(CN)_6^{4-}$, Ce(IV), etc.), because chemiluminescence arises most frequently from oxidation reactions involving large energy changes. Between them, $KMnO_4$ is presented as the most efficient oxidant for direct

liquid phase chemiluminescent processes [26, 27]. The excellent behaviour of potassium permanganate associated to direct chemiluminescence procedures should be due to an unusual case of phosphorescence at room temperature, in which is an excited manganese (II) emitting species of unknown constitution seems to be the emitter responsible [28,29].

The flow assembly used is depicted in Fig.2.a). The pattern flow employed in preliminary studies is described in Fig.3.a) All pesticides were tested with the lamp OFF and ON. All solutions were aspirated at a flow rate of 10 mL min^{-1}.

The obtained results are summarised in Figure 4. Either absence of chemiluminescence or a very weak chemiluminometric response (≤ 3 x background noise) was obtained with lamp OFF in all media except H_2O_2 for which a clear analytical signal was observed. Nevertheless, UV-photo-irradiated imidazolinone turned into strong chemiluminescent compounds in all media after irradiation. Imazethapyr, however, provided very weak chemiluminescence intensities or indistinguishable from background noise, even with photo-irradiation. Finally, deionized water was selected as medium of photodegradation in response to the simplification of the chemical system, the absence of analytical signal with the lamp OFF, and the highest outputs observed.

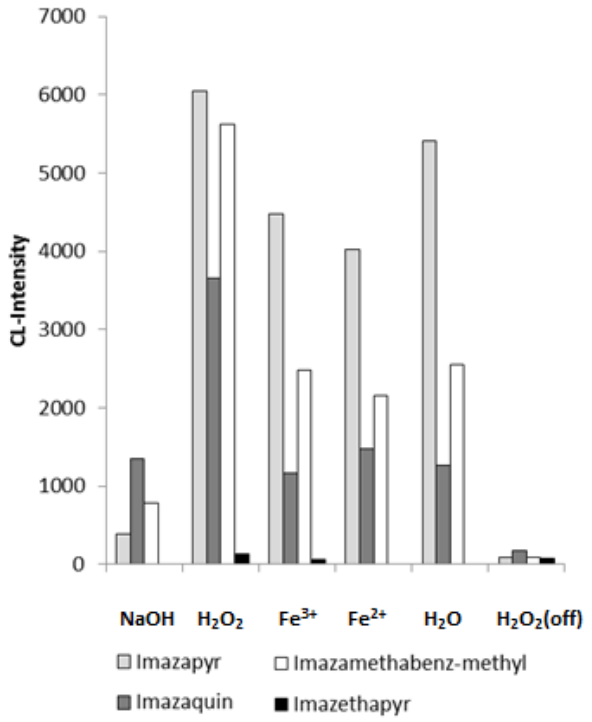


Fig. 4 Influence of photodegradation media on CL-intensity.

The obtained results were consistent with those reported in literature. In sharp contrast to the slow hydrolytic degradation and a rather stability in the dark of imidazolinones, they are photodegradated rapidly and extensively in aqueous solution. Moreover, UV-light causes a quantitative degradation of imidazolinones [30, 31].

The photochemical degradation scheme of imazapyr and analogous imidazolinones seems to be very similar as result of the study performed in aqueous solution by means of liquid chromatography coupled with mass spectrometry.

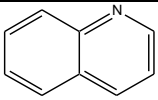
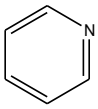
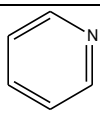
Herbicide	*Aromatic Ring*	R_1	R_2
Imazamox		CH_3OCH_2	H
Imazapyr		H	H
Imazaquin		H	H
Imazametha benz-methyl		5-Me/6-Me	Me
Imazapic		5-Me	H
Imazethapyr		5-Et	H

Table 1 Chemical structure of imidazolinone pesticides.

The photoproducts occurring during the UV irradiation indicate that degradation of imidazolinones upon UV irradiation occurred mainly at the imidazolinone ring and it leads to pyridine derivatives [32].

Subsequent studies of chemical and flowing parameters were carried out employing a 20 mg L^{-1} aqueous solution of imazapyr as test substance.

3.2. Optimization of the oxidant concentration

The concentration of the oxidant is a very critical variable in direct chemiluminescent systems. A too low concentration of oxidant reagent can decrease the chemiluminescent signal until it becomes undetectable, while high concentrations can lead to associated problems of self-absorption of the chemiluminescent emission by the same oxidant. The influence of the $KMnO_4$ concentration was examined over the range $2\ 10^{-3} – 8\ 10^{-5}$ mol L^{-1}. A maximum chemiluminescence intensity was observed for $2\ 10^{-4}$ mol L^{-1} prepared in 2 M sulphuric acid.

3.3. Study of photosensitizers and CL-enhancers

The influence of various photosensitizers and/or CL-enhancers was studied. These compounds can be divided in the following groups attending their function: a) compounds generating o stabilizing free radicals potentially favouring a radical mediated photodegradation mechanism (e.g.dioxane, dimethylformamide, acetone, formic acid, acetonitrile, THF, ethanol [33, 34]; b) compounds providing organized media and structural rigidity to the medium, which act increasing the lifetime of the emitting specie (β-cyclodextrins, anionic,

cationic and neutral surfactants: SDS, hexadecylpyridinium, Triton X-100, respectively) [35]; and, c) substances frequently used in chemiluminescence as sensitizers and then enhancing the emission intensity due to an energy transfer mechanism (e.g. Rhodamine B and 6G [36], and quinine [37]).

Q_1 (deionized water as blank or pesticide), Q_2 (photosensitizer/CL-enhancer), Q_3 (oxidant) and Q_4 (deionised water) were aspirated according with the following multi-insertion cycle: V1 = 50*(0.4,0.2); V2= 30 (ON), 150 (OFF), 50*(0.6,0.1); and V3= 180 (OFF), 35 (ON) (see Fig.2 and 3). All compounds were tested with the lamp ON and OFF. Similarly, they were obtained blank outputs (pesticide solution was replaced by deionized water) with the lamp ON and OFF. This allowed assessing the influence of the tested sensitizer on the photodegradation step as in the chemiluminescence reaction.

Quinine 0.015%, Triton X-100 0.5 %, hexadecylpyridinium 5 10^{-4} M, acetone 0.5%, dimethylformamide 5%, dioxane 5 %, formic acid 5%, THF 5 %, Rhodamine B and 6G 5 10^{-4} M, and ethanol 5 % yielded analytical signals of the same order for blank and pesticide solutions with lamp ON. SDS 0.15 %, β-cyclodextrins 10^{-5} M and acetonitrile 5% showed low blanks and a significant increase of chemiluminescent response by UV irradiation of the pesticide. The best results (ratio lamp ON pesticide/lamp ON blank) were obtained with acetonitrile 5 % (ratio pesticide/blank was 150), thus acetonitrile was selected as photosensitizer and the concentration was optimized over the range 5-40 %. The higher the concentration of acetonitrile was higher was the increase in the signal of the blank solution. Finally, acetonitrile 5 % was selected as optimum.

3.4. Influence of time of stopped flow

As results of changes in photodegradation medium and previously to the optimization of flow parameters, the time of stopped flow was optimized over the range 120-270 s. An increase of about 30% was observed for 270 s of photodegradation against the signal obtained with 180 s, time for which previous experiments were performed (see Fig.5).

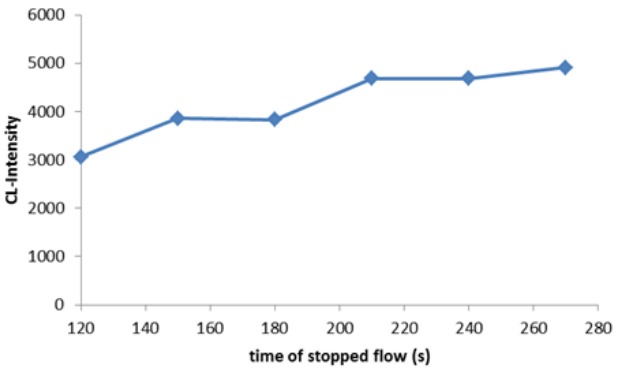


Fig. 5 Influence of UV photo-irradiation time.

3.5. Optimization of flow-rate and insertion profile

This variable was examined over the range 7.1-12.8 mL min^{-1}. Flow-rates lower than 7.1 mL min^{-1} was discarded due to the fast kinetic of the chemiluminescent reaction. The increase in flow rate resulted in an increase in the CL-intensity, however, also occurred in the same sense a significant increase in the irreproducibility. The pulsed flow provided by the peristaltic pump at high flow-rates affected seriously the reproducibility of micro-insertions of reagents and the subsequent mixture in photo-reactor and flow-cell. The selected flow rate for aspirating sample and reagent solutions was 10 mL min^{-1}, for which the best compromise between analytical signal and reproducibility was obtained (see Fig.6)

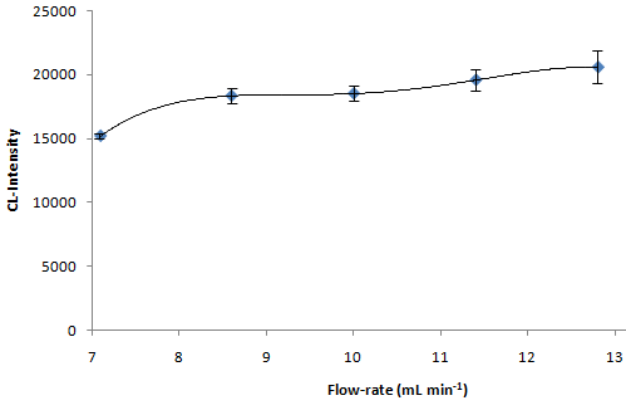


Fig. 6 Influence of flow-rate.

The effectiveness by mixing sample and reagent solutions can be controlled in the flow manifold via software. V1 controls the mixture of pesticide and medium of photodegradation in the photoreactor, V3 the mixture of oxidant and CL-enhancer, and V2 the alternated multi-insertion of photodegradated pesticide and CL- reagent. The optimization of the insertion profile permits to find for each solenoid valve the best combination N*(t_1, t_2), where t_1 is the time of valve in ON, t_2 is the time of valve in OFF, and N is the number of cycles ON/OFF. For each valve and independently it was optimized and by this order, first N, next t_1 and t_2 (different combinations maintaining the total inserted volume were tested, $t_1 + t_2$ = constant), and finally, again, t_1 and t_2, maintaining the optimal ratio t_1/t_2 = constant. Usual ranges examined were as follows: N (30-70), t_1 and t_2 (0.1-0.9 seconds). It is very convenient to insert a large sequence of sample-medium segments (N), mainly due to the large length of the photo-reactor (150 cm) and to assure an effective mixture of the photo-reactor effluent with the mixture of the reagents (oxidant and enhancers) for the chemiluminometric process. Values of $t_1/t_2 > 1$ in V1 and V2 avoided the excessive dilution of the pesticide in the flow system. Excellent reproducibility was obtained for times of insertion as short as 0.1 second, equivalent to the insertion of 16 µL of solution. Selected values are shown in Fig.3b).

4. Analytical applications

A comparison of the analytical features of the methods for determination of imazapyr, imazaquin and imazamethabenz-methyl are summarized in Table 2. The day-to-day reproducibility was obtained as the RSD of the slope of four different calibration graphs obtained in different working sessions. The repeatability was calculated at two different concentration levels (0.5 and 3 mg L^{-1}) for a series of 10

insertions of each pesticide. The limit of detection was defined as 3 x RSD of the base line (no blank peaks were obtained), and was experimentally determined by decreasing the analyte concentration until this relationship was reached. The sample throughput was calculated using the same standards concentration employed in the repeatability study.

Figure 7 shows a calibration (response chart) for imazapyr over the range 0.1-10 mg L^{-1}, and the shape of peaks.

Analytical Parameter	*Imazapyr*	*Imazaquin*	*Imazabenzmethyl*
Equation (C in mg L^{-1})	$I_{CL} = 300\ C + 253$ ($r^2 = 0.992$)	$I_{CL} = 349\ C + 191$ ($r^2 = 0.996$)	$I_{CL} = 168\ C + 236$ ($r^2 = 0.993$)
Linear range (mg L^{-1})	0.05-10	0.1-10	0.01-10
Day-to-day reproducibility on the slope RSD (%)	12.8	1.1	8.0
Limit of detection (mg L^{-1})	0.05	0.1	0.01
Repeatability[1] RSD(%) (n=10)	1.3/5.2	2.2/2.8	1.4/3.1
Sample throughput (h^{-1})	12	12	12

Table 2 Analytical features. I_{CL}: Chemiluminescence intensity (counts). [1]At 0.5 and 3 mg L^{-1}.

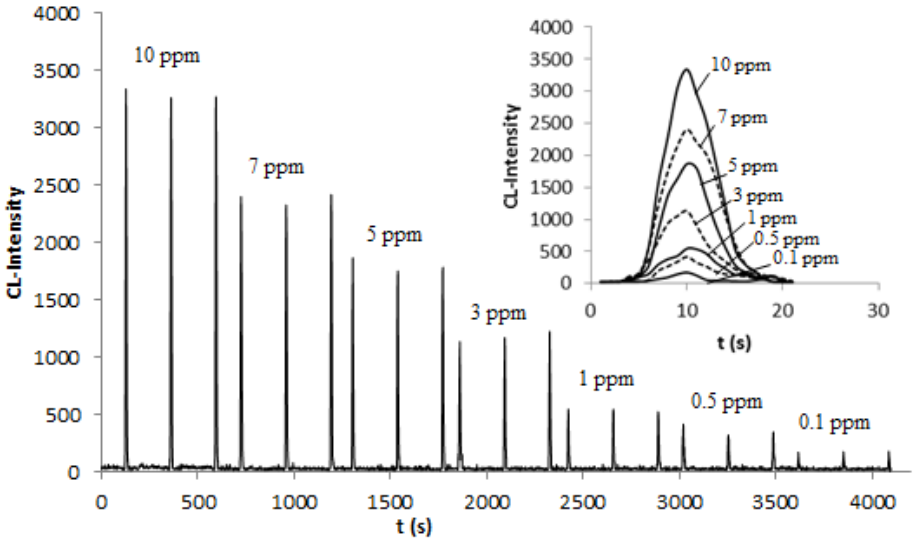


Fig. 7 Calibration for imazapyr and shape of analytical peaks.

The influence of potential interfering species accompanying imidazolinone pesticides in real samples (*viz.* metal ions and common inorganic ions) was studied using solutions containing 2 mg L^{-1} of pesticide and decreasing concentrations of each tested species. The signals thus obtained were compared with that provided by the pure pesticide solution in order to determine the relative errors resulting from the presence of the foreign species. Table 3 shows the concentration ratio tested compound/pesticide in mg L^{-1} for which no interference was observed.

The interfering effect of divalent cations can be explained on the basis of the chelating properties of imidazolinones. The chelating set active involves rather weak donors, namely the pyridine (imazapyr) or quinoline (imazaquin) and imidazole nitrogens. The lactam site of the imidazolinone ring can deprotonate and the ligand takes advantage of a rather basic nitrogen atom, which, assisted by the pyridine or quinoline donor, yields stable complexes increasing coordination at the metal ion [38, 39]. Complexation reactions affect the stability of imidazolinones against UV-degradation as well as the susceptibility for yielding chemiluminiscent photo-products.

Interferent	*Imazapyr*	*Imazaquin*	*Imazamethabenz-methyl*
Na^+	1000	1000	1000
K^+	<0.1	1000	1000
Ca^{+2}	<0.1	1000	1000
NH_4^+	1000	<0.1	100
Mg^{+2}	1000	<0.1	<0.1
Mn^{+2}	<0.1	100	1000
Cu^{+2}	100	<0.1	<0.1
Zn^{+2}	<0.1	<0.1	500
Cl^-	<0.1	1521	1521
SO_4^{-2}	<0.1	<0.1	2086
CH_3COO^-	3105	3105	<0.1
HCO_3^-	<0.1	<0.1	<0.1
NO_3^-	<0.1	<0.1	<0.1

Table 3 Study of interferences.
In Table concentration ratio (tested compound/pesticide) for which no interference was observed (± 5% of standard response).

The proposed method was applied to the analysis of spiked tap and mineral water samples. The results obtained are shown in Table 4.

Spiked samples		*Mineral water*		*Tap water*	
Pesticide	Added (mg L^{-1})	Found (mg L^{-1})	Error (%)	Found (mg L^{-1})	Error (%)
Imazapyr	0.5	0.53	+6.0	0.40	-20.0
	3.0	3.26	+8.7	3.25	+8.3
	5.0	5.13	+2.6	5.12	+2.4
Imazaquin	0.5	0.45	-10.0	0.46	-0.8
	3.0	2.87	-4.3	2.89	-3.7
	5.0	5.23	+4.6	5.1	+2.0
Imazamethabenz-methyl	0.5	0.47	-6.0	0.43	-14.0
	3.0	3.02	+0.7	2.96	-1.3
	5.0	4.65	-7.0	4.66	-6.8

Table 4 Determination of imidazolinone herbicides in mineral and tap water.

5. Conclusions

A fully automated procedure for the determination of imidazolinones in waters is described. The method is based on the multi-commutation approach. It provides a simpler and more efficient automation of the flow-analytical procedures than FIA. Hydrodynamic characteristics of the flow manifold can be easily controlled *via* software by resetting the duration of the electrical pulses switching the valves on and off or by altering their commutation sequence.

The photolysis provided by low-pressure mercury lamps in photodegradation processes permits to increase the number of compounds of environmental interest susceptible of determination by direct chemiluminescence (even compounds which exhibit null or very weak chemiluminiscent behaviour), thanks to the chemiluminescent properties of the resulting photo fragments. Despite the short time of photo-irradiation (270 seconds), dramatic differences were observed for imazapyr, imazaquin, and imazamethabenz methyl, which led to strong chemiluminescent photoproducts.

From author´s knowledge is the first time that a chemiluminometric analytical procedure for determination of imidazolinone herbicides has been reported.

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