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Determination of *N*-methylcarbamate pesticides using flow injection with photoinduced chemiluminescence detection

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Abstract

A sensitive, economic, rapid and simple method for the determination of four *N*-methylcarbamate pesticides: methomyl (2.0-80 ng mL^{-1}), aldicarb (5.0-50 ng mL^{-1}), butocarboxim (2.0-60 ng mL^{-1}) and oxamyl (2.0-60 ng mL^{-1}); is reported. It relies on the coupling of photoinduced chemiluminescence (PICL) detection with flow injection (FI) methodology. The automation of FI together with the use of light as a reagent decreased the environmental impact of the analysis. The proposed method was based on the oxidation of these pesticides, previously irradiated on-line with UV light, with cerium(IV), using quinine as a sensitizer. Limits of detection below the legal limits (100 ng L^{-1}) established by the European Union for drinking waters were obtained without the need of preconcentration steps. A good inter-day reproducibility (1.6-6.4 %, n=5), repeatability (rsd=2.7 %, n=25) and high throughput (123 h^{-1}) were achieved. The method was successfully applied to the determination of methomyl in natural waters with mean recoveries ranging from 90 to 98%.

Keywords: Photoinduced chemiluminescence; flow injection; *N*-methylcarbamates; pesticides; water.

1. Introduction

The rapid biodegradation of carbamate pesticides has resulted in their broad use as insecticides, although they can also be used as herbicides, acaricides, fungicides and nematocides. As they are highly soluble in water, their residues may be widely distributed in aquatic systems through runoff and leaching from soil into ground and surface waters [1]. Consequently, it is of great interest the development of new analytical methods for the determination of carbamates in environmental samples.

Liquid chromatography (LC) has become the preferred choice for the determination of carbamates [2,3] because of the thermal lability of these pesticides, which makes difficult the use of direct gas chromatographic (GC) methods. Methods of detection such as fluorescence [4] and UV [5] have been used, but mass spectrometric (MS) detectors have resulted in greater likelihood of identification and are acknowledged to be extremely useful and authoritative for determination of pesticide residues [6]. But in spite of the powerful analytical capabilities of those methods, problems have arisen from the presence of co-eluting matrix, which can severely affect important method parameters such as limit of detection, linearity, accuracy and precision. That problem, called matrix effect, has made necessary the introduction of different calibration methods to address that drawback [7]. Capillary electrophoresis (CE) is another interesting alternative for the determination of carbamates, but this technique is limited by its low sensitivity, which is derived from both, the low sample volume injected and the very limited optical path length employed for on-capillary detection [8].

Chemiluminescence (CL) has been successfully coupled with LC for the monitoring of a wide variety of compounds in diverse fields such as environmental and food analysis;

representing an alternative to other powerful detection modes as MS in terms of sensitivity. Low cost and simplicity of the required instrumentation are other advantages of CL detectors [9]. Hence, several LC/CL methods have been developed for the determination of *N*-methylcarbamates [10-12].

The analysis of pesticides can also be readily accomplished by the coupling of CL detection with flow injection (FI) [13-18]. FI is a simple and inexpensive technique, which using common instrumentation offers an increased sampling-rate, low reagents consumption and high precision and versatility [19]. Moreover, it is particularly well suited to monitoring transient light emission from CL reactions, since it allows irradiation time to be easily controlled. In addition, the sample is processed under reproducible conditions, allowing its isolation from the environment and avoiding external contamination [20]. Hence, flow-based luminescence-sensing methods show high potential for analysis of residues in aqueous environment [21], and the development of chemical sensors for environmental analysis based on fluorescence, phosphorescence and CL signals continues to be a dynamic topic within the sensor field [22].

In this context, the present paper deals with a simple, rapid and sensitive method for the determination of four *N*-methylcarbamates, namely methomyl, oxamyl, butocarboxim and aldicarb; without the need of sophisticated and expensive equipment and fast enough for use in environmental control of pollutants. The proposed photochemically induced chemiluminescence (PICL) method took advantage of the use of light as a reagent, avoiding the addition of large concentrations of pollutant reagents minimizing the cost and environmental impact of analysis. That fact together with other advantages such as shorter reaction times and improved sensitivity and selectivity has greatly increased the applicability of PICL [23,24].

The proposed method was based on the CL reaction between the photoproducts of the above-mentioned pesticides and cerium (IV) in acidic medium using quinine as a sensitizer. It

was successfully applied to the determination of methomyl in natural waters at low concentrations (5.0-40 ng mL^{-1}), without the need of preconcentration steps.

2. Experimental

2.1 *Reagents and solutions*

All solutions were prepared from analytical-grade reagents in Milli-Q water (18 MΩ cm^{-1}) from Millipore, Bedford, MA, provided with a 0.22 μm fiber filter. Methomyl (99.5%) was supplied by Chem Service. Ziram (97%) and paraquat (99.5%) were obtained from Dr Ehrenstorfer GmbH. Butocarboxim (99.2%), amitrole (99.9%), acetamiprid (99.9%), 2,4-D (99.6%), diuron (99.5%), cyromazine (99.9%), carbaryl (99.8%), diquat monohydrate (99.4%), glyphosate (99.2%), fluroxypyr (99.2%), fenamiphos (97.7%), imazalil (99.8%), metalaxyl (99.9%), MCPA (98.7%), pirimicarb (99.6%) and quinmerac (99.2%) were purchased from Riedel-de Haën. Aldicarb (99.9%), oxamyl (99.5%), chloridazon (99.9%), metazachlor (99.9%) and myclobutanil (99.4%) were supplied by Fluka.

Stock solutions of methomyl (100 mg L^{-1}) were prepared in water and stored at 4ºC. They remained stable for at least 1 month as expected for neutral pH [25]. The stock solutions of the other pesticides were used within 24 h, since they hydrolyze faster than methomyl at pH 7 [25]. Quinine stock solutions ($1.0x10^{-3}$ M) were prepared weekly; dilutions of them were prepared in NaOH 0.20 M immediately before analysis. Ce(IV) solutions were freshly prepared in H_2SO_4 0.13 M or water (when $HClO_4$ was used as oxidation medium).

2.2 *Apparatus*

The flow assembly used is depicted in Figure 1 and consisted of 0.8 mm i.d. PTFE coil; a Gilson (Worthington, OH, USA) minipuls peristaltic pump provided with pump tubing from Omnifit; and a Model 161T031 valve (NResearch, Northboro, MA, USA). The flow cell was a flat-spiral glass tube of 1 mm i.d. and 3 cm total diameter. The photodetector package was a

P30CWAD5 type 9125B photomultiplier tube supplied by Electron Tubes (Uxbridge, UK), located in a laboratory-made light-tight box to avoid light input. The output was transferred to a computer equipped with a counter-timer, also supplied by Electron Tubes.

In order to carry out the photodegradation, a photoreactor was added. It consisted of a 400 cm length and 0.8 mm i.d. PTFE tubing helically coiled around a 15 W low-pressure mercury lamp (Sylvania) (G1578) for germicidal use.

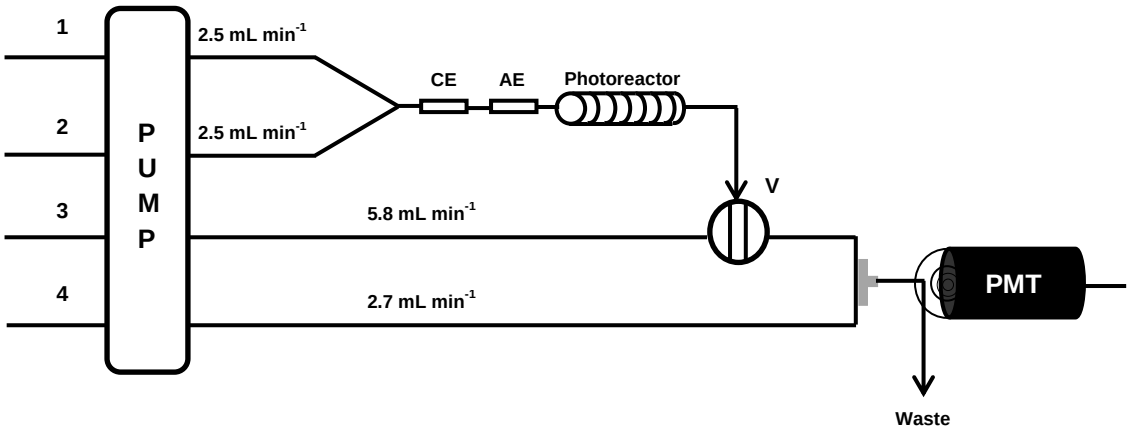


Figure 1. Flow assembly used for the determination of methomyl.
CE, cationic exchanger; AE, anionic exchanger; V, injection valve; PMT, photomultiplier tube.
1, Methomyl.
2, NaOH 0.20 M + quinine $2.0x10^{-5}$ M.
3, Water.
4, Cerium(IV) $2.5x10^{-4}$M/H_2SO_4 0.13 M.

2.3 *Sample preparation*

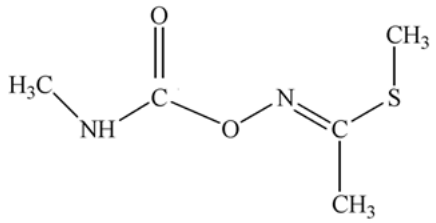
Spring and tap waters were collected in plastic flasks and immediately filtered with 0.45 µm polyamide membrane filters (Sartorius, Goettongen, Germany). Spring waters were stored in glass flasks protected from light at 4 ºC in the refrigerator. Tap and mineral waters were immediately analysed and the analysis of spring waters was carried out within 48 h. In all cases, a $1.0x10^3$ ng mL^{-1} stock solution of methomyl was employed to obtain by dilution concentrations within the linear range of the method, namely**,** 5.0, 10, 20, 30 and 40 ng mL^{-1}.

Ionic interferences were removed on-line using ion-exchange resins: Duolite C206A (cationic) and IRA-400(OH) (anionic). The exchangers were prepared by packing Omnifit 15 cm x 3 mm i.d. glass columns with the above-mentioned resins.

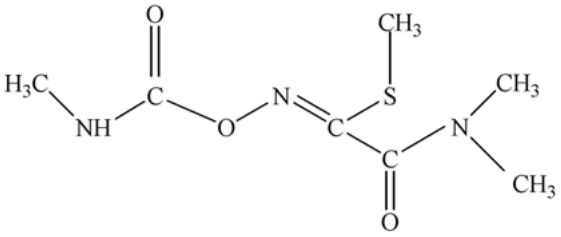
3 Results and discussion

3.1 *Preliminary studies: selection of the oxidant system and photodegradation conditions*

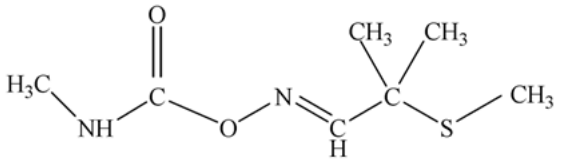
Methomyl (Figure 2) was the pesticide selected for the optimization step. It is an insecticide widely used for control of a broad spectrum of arthropods on various field crops ranging from fruits to tobacco (estimates for the period between 2001 and 2007 show annual average usage of 363000 kg in US [26]). Moreover this pesticide is the principal degradation product of the insecticide thiodicarb; consequently, methomyl is expected to be present at high levels in water [27]. Although methomyl does not exhibit CL, previous studies based on molecular connectivity [28] had demonstrated that there was a high probability that the oxidation of the photodegraded pesticide shows CL response. Therefore, to induce photodegradation, an irradiation source was incorporated to the manifold (Figure 1). It consisted of a low-pressure Hg lamp which emitted over the range 200-300 nm and maximally (roughly 85 % of all light) at 254 nm (methomyl shows a maximum absorbance at 231 nm). When a dilute aqueous solution of methomyl is irradiated with UV light at 254 nm, acetonitrile, dimethyl sulphide, acetone, *N*-ethylidenemethylamine and carbon dioxide are produced [29].



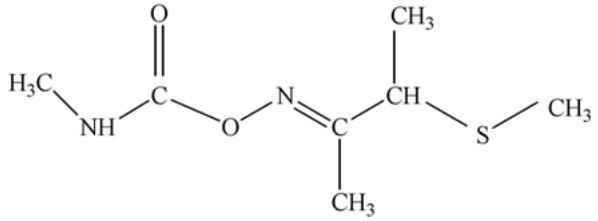
Methomyl



Oxamyl



Aldicarb



Butocarboxim

Figure 2. Chemical structure of the *N*-methylcarbamates analyzed.

The following oxidants: $KMnO_4$ 2.0x10^{-4} M, and Ce(IV), KIO_4, $K_2S_2O_8$, $K_3Fe(CN)_6$, *N*-bromosuccinimide and H_2O_2, all of them at 5.0x10^{-4} M, were tested with and without irradiation. H_2SO_4 1.0 M was used as oxidation medium for all oxidants; except for $K_3Fe(CN)_6$ and H_2O_2, in those cases NaOH 2.0 M was the medium employed; both oxidation media were

assayed for KIO_4. On the other hand, water, H_2SO_4 0.10 M and NaOH 0.20 M (1.0 mL min^{-1}) were tested as photodegradation media and mixed with 100 mg L^{-1} of methomyl (1.0 mL min^{-1}). The manifold used was very similar to that depicted in Figure 1, but one additional channel (channel 5) was added, and the solutions flowing by channels 4 and 5 were mixed using a T-piece. The oxidants were introduced by channel 4 and the oxidant media by channel 5 at the same flow rate (1.2 mL min^{-1}). Water was used as a carrier (channel 3: 5.0 mL min^{-1}).

As a result, no significant response was observed without previous irradiation of the pesticide and the highest PICL intensities were achieved for $KMnO_4$ and Ce (IV), the acidic (H_2SO_4 0.10 M) and basic medium (NaOH 0.20 M) being the best photodegradation media for $KMnO_4$ and Ce(IV), respectively. After that, the concentrations of both oxidant systems were changed over the ranges ($5.0x10^{-6}$-$4.0x10^{-4}$) M for $KMnO_4$ and ($5.0x10^{-5}$-$1.0x10^{-3}$) M for Ce (IV). The best results for methomyl 25 mg L^{-1} were achieved using $KMnO_4$ $2.0x10^{-5}$ M (3.4 a.u.) and Ce (IV) $5.0x10^{-4}$ M (10 a.u.); consequently, Ce(IV) was used for further studies.

The influence of different oxidation media: H_2SO_4, $HClO_4$, H_3PO_4, HNO_3, HCl and CH_3COOH at 1.0 M was studied. The best results were achieved for sulfuric and perchloric acids. Further experiments were carried out using (0.50-4.0) and (0.25-2.0) M ranges for $HClO_4$, and H_2SO_4, respectively. As a result, $HClO_4$ 2.0 M was the medium selected, although the CL signal achieved using H_2SO_4 1.0 M was very similar.

The influence of the NaOH concentration used as photodegradation medium was also investigated over the (0.020-2.0) M range. It was introduced by channel 2, while methomyl was introduced by channel 1 (Figure 1). Finally, 0.20 M was selected as the optimum concentration.

3.2 *Optimization*

There are a variety of compounds that can enhance the CL emission through several ways such as energy transfer processes, promotion of the photodegradation step, free radicals generation; or providing structural rigidity to the medium, which increases the lifetime of emitting species.

Because of that, the effect of several of ,common enhancers on the CL signal was studied using the conditions set in the preliminary studies. The compounds and concentrations tested were: quinine, sulfite, 8-hydroxyquinoline, riboflavin, and fluorescein (all of them at $1.0x10^{-4}$ M); formic acid (0.50%), ethanol (5.0%), acetone (1.0%), acetonitrile (20%), acetone (1.0%) + acetonitrile (20%), 2-propanol (20%), dioxane (10%), rhodamine B ($1.0x10^{-6}$ M) and yellowish eosin ($1.0x10^{-6}$ M). The effect of anionic, cationic and neutral surfactants, introduced before and after the photoreactor, were also tested using two concentrations (above and below critical micelle concentrations). The substances and concentrations selected were: sodium dodecyl sulfate (0.15 and 2.9%), hexadecylpiridinium (0.022 and 0.43%), triton X-100 (0.12 and 2.4%) and β-cyclodextrin (0.14 and 2.8%). No improvement in the CL signal was obtained; actually, in most cases a negligible difference with respect to the blank signal was observed; consequently, the use of surfactants was discarded.

It was found that only the introduction of quinine ($1.0x10^{-4}$ M) and fluorescein ($1.0x10^{-4}$ M) before the photoreactor increased the CL signal. The observed increases were 446% and 100% for quinine and fluorescein, respectively. In order to select the best sensitizer, their concentrations were changed over the ($2.0x10^{-5}$-$1.0x10^{-3}$) M and ($1.0x10^{-5}$-$1.0x10^{-3}$) M ranges for quinine and fluorescein, respectively. The enhancing effect of these substances on the CL response is shown in Figure 3. As can be observed, the increase achieved in the CL intensity was very important in both cases, leading to more than a 5-fold and a 2-fold increase for quinine and fluorescein, respectively. Bearing in mind the highest CL signal achieved with quinine, fluorescein was discarded, and quinine $2.0x10^{-5}$ M in NaOH 0.20 M was introduced in channel 2 for further experiments.

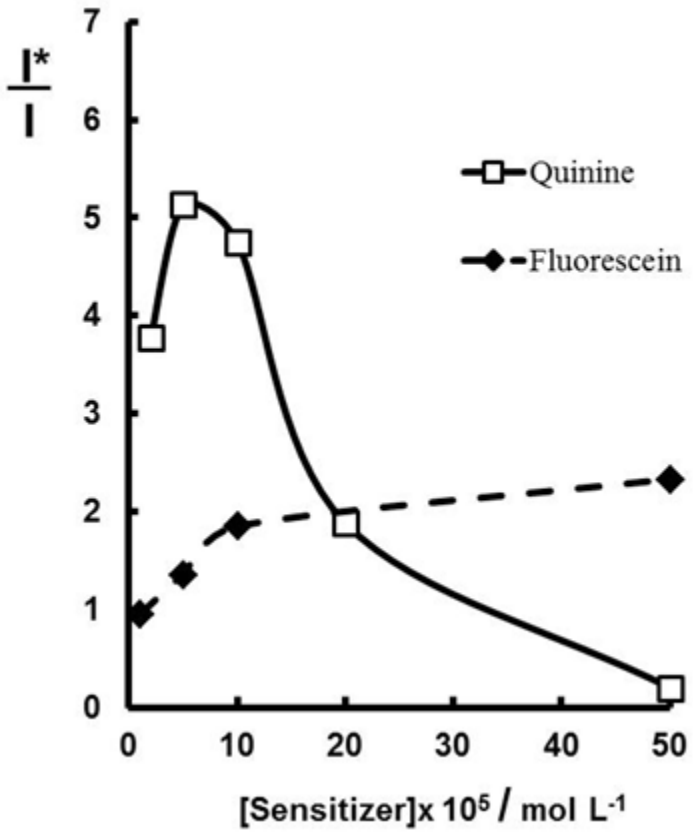


Figure 3. Variation of methomyl PICL signal achieved using enhancers.
I*, CL signal with sensitizer
I, CL signal without sensitizer

The effect of sample volume on the analytical signal was studied by changing its value between 200 and 700 µL. It was observed that CL response increased sharply up to 500 µL and levelled off for higher inserted volumes; consequently, that value was selected as the optimum.

The effect of the temperature on the oxidation and photodegradation steps was also studied changing from room temperature to 60 ºC. A dramatic decrease in the CL intensity was observed when the oxidation of the photoproduct of methomyl took place at high temperatures. On the other hand, the influence of temperature on the photodegradation step was negligible. Consequently, room temperature was selected.

The effect of the total carrier and oxidant flow rates on the CL response was studied keeping its ratio (2.1:1) constant, in order to avoid changes in the final optimized concentrations at the detector. This parameter resulted to be very important as shown in Figure 4. As can be observed, the CL intensity increased sharply until a total flow rate value of 5.0 mL min^{-1}; however, above 9.0 mL min^{-1} a dramatic drop in the signal was observed. Consequently, a total flow rate of 8.5 mL min^{-1} (5.8 and 2.7 mL min^{-1} for carrier and oxidant, respectively) was selected.

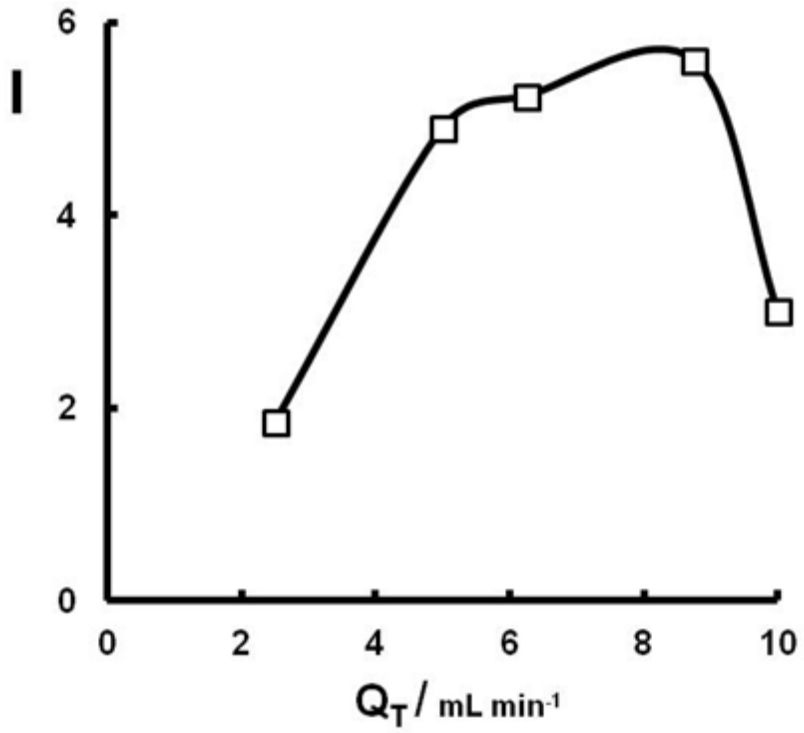


Figure 4. Effect of the total flow rate (Q_T) at the detector on the methomyl PICL signal

The influence of the irradiation time on the analytical signal was also investigated. The range studied for the total flow rate (channels 1 and 2 of the manifold depicted in Figure 1) was over (2.0-6.0) mL min^{-1}, which corresponded to (60-20) s irradiation time. A total flow rate of 5.0 mL min^{-1} (24 s of irradiation time) was the optimum.

Finally, the effect of photo-Fenton system (H_2O_2/Fe^{2+}/UV), which causes a rapid degradation of methomyl via hydroxyl radicals, was also investigated using the optimum conditions established by Tamimi et al. [30] for the degradation of this pesticide, Fe(II) 0.50 mM and H_2O_2 1.0 mM at pH 3.0. Hence, Fenton reagent together with quinine was introduced and mixed with 0.50 ng mL^{-1} methomyl before irradiation. The result was a dramatic decrease in the analytical signal; consequently, its use was discarded.

3.3. *Mechanism for the CL reaction*

The possible CL reaction mechanism for the oxidation with Ce(IV) in the presence of quinine has been reported by several authors [31-33]. According to them, the reduction of Ce(IV) would produce excited Ce(III), which is deactivated by emitting light of 350 nm yielding a weak CL signal.

In the presence of quinine, excited Ce(III) would transfer energy to quinine yielding excited quinine. Quinine is a good fluorescent substance (Φ=0.577) having an emission maximum at about 450 nm [34]. Consequently, quinine can give a strong light emission in the wavelength range of 400-500 nm, which makes that the CL intensity is greatly increased.

3.4 *Reoptimization*

In preliminary studies perchloric and sulfuric acids provided very similar results when assayed as oxidation medium. Because of that, their influence on the CL intensity was studied again by changing their concentrations over the ranges (0.25-2.0) and (0.10-2.0) M for $HClO_4$ and H_2SO_4, respectively. That experiment revealed that highest signals were obtained using H_2SO_4 0.25 M under the new experimental conditions set in the optimization step. That 8-fold decrease achieved in the acid medium concentration led to a considerable improvement in the cost and environmental impact of the analysis. In addition, it made possible to eliminate one channel in the manifold, since Ce(IV) was stable in the new oxidation medium selected.

3.5 *Analytical performance*

3.5.1 Analytical data

Further investigation demonstrated that under the selected experimental conditions, other *N*-methylcarbamate pesticides namely, aldicarb, butocarboxim and oxamyl (Figure 2) provided high PICL responses. Because of that, the analytical performance of the method was evaluated for all these pesticides. The obtained results are shown in Table 1.

Table 1. Analytical figures of merit for *N*-methylcarbamates determination.

	Linear equation[a] (C, ng mL^{-1})	Dynamic range (ng mL^{-1})	LOD (ng L^{-1})	Reproducibility[b] (RSD, n=5)
Methomyl	I_E=0.143 C + 0.269	2.0–80	50	3.2%
Aldicarb	I_E=0.112 C + 0.140	5.0–50	50	6.4%
Butocarboxim	I_E=0.097 C + 0.156	2.0–60	50	1.6%
Oxamyl	I_E=0.083 C + 0.263	2.0–60	100	2.2%

a. I_E= Intensity of emission; C= concentration of pesticide.

b. Values obtained from the slopes of 5 calibration graphs made on different days.

LOD= Limit of detection.

The calibration graphs were constructed using five injections from eight concentrations. The limits of detection were determined by decreasing the concentration of the pesticides till the signal was the average blank peak height plus 3xSD. The interday reproducibility was estimated by the relative standard deviation calculated for the slopes of calibration graphs performed in five different days with freshly prepared solutions.

Finally, the repeatability of the proposed method was tested by inserting a series of 25 standard solutions containing 40 ng mL^{-1} of methomyl. As a result of that experiment the RSD for the CL response obtained was 2.7% and the throughput was established in 123 h^{-1}.

3.5.2 Comparison with other methods

As mentioned in the introduction section, LC methods are the preferred option for carbamates detection. On the other hand, coupling with FI methods offers several advantages as low reagents consumption and simplicity. Taking advantage of this, a method based on sequential injection hyphenated to LC with UV detection and micro-solid phase extraction was reported for carbamates determination [35]; but despite enrichment factors ranging from 20 to 125, the sensitivity was poor, with limits of detection within the $(0.10\text{-}2.0)x10^4$ ng L^{-1} range. The same authors developed a new approach based on ultrasound-assisted surfactant-enhanced emulsification microextraction for the preconcentration of carbamate pesticides prior to HPLC analysis [36]. Hence, enrichment factors between 100 and 200-fold were obtained, which led to limits of detection in the range of $(0.10\text{-}5.0)x10^3$ ng L^{-1}.

The developed method is also competitive in terms of sensitivity with LC methods coupled with other detectors as shown in Table 2. Among the most recently published LC/MS existing methods for carbamates determination in aqueous samples, those in which at least 3 of the studied pesticides were determined were selected for comparison [37,38]. As can be observed in Table 2 they provided similar results to those obtained with the proposed method.

296 Table 2. Comparison of the proposed method with other analytical methos.

297

Method	Preconc Factor	LOD (ng L^{-1})	Reference
LC/CL	3000	39-58	[10]
	1000	3.9-37	[11]
LC/MS	250	10-50	[37]
	0	(0.41-2.8)x10^3	[38]
CE/MS	10	(1.0-3.0)x10^4	[39]
	10	7.3-14	[40]
Proposed method	0	50-100	-

298

299 On the other hand, the LC/CL methods reported up to now for analysis of carbamates
300 needed solid phase extraction, using high volumes of sample, 1.5 L [10] and 0.50 L [11] in
301 order to achieve sensitivity levels below the legal maximum concentration permitted.

302 Finally, when CE , an interesting alternative in terms of selectivity, was used for the
303 analysis of methomyl, oxamyl, aldicarb and other *N*-methylcarbamates [39,40] the sensitivity
304 decreased.

305 *3.5.3 Interferences*

306 The influence on CL signals of urea, a common organic pollutant in environmental samples, and
307 the most commonly present ions in natural waters, was studied by preparing solutions of 40 ng
308 mL^{-1} of methomyl and decreasing the concentration of the potential interferences. The tolerance
309 of each foreign species was taken as the largest amount to yield a variation of less than ± 5.0%
310 in the analytical signal. As can be observed in Table 3, some of the ions tested interfere
311 significantly at their common concentrations in natural waters. Interferences from HCO_3^- and
312 Mg^{2+} were especially relevant, given the high common concentrations of these ions in natural
313 waters.

Table 3. Study of interferences of urea and ions on 40 mg L^{-1} methomyl PICL signal.

Interference	mg L^{-1}	Error, %
Ca^{2+}	200[a]	-1.8
Mg^{2+}	20	4.7
Na^{+}	1000	3.2
K^{+}	5000[a]	-1.8
NH_4^{+}	2	-2.5
SO_4^{2-}	1000	-3.8
Cl^{-}	100	3.1
HCO_3^{-}	25	-4.2
$H_2PO_4^{-}$	1000[a]	3.6
HPO_4^{2-}	1000[a]	4.3
CH_3COO^{-}	10	-3.4
NO_3^{-}	1	-4.8
Urea	25	-4.3

a. Maximum concentration assayed.

On the other hand, the influence of other pesticides on the CL signal of 40 ng mL^{-1} of methomyl was also tested. Hence, 19 pesticides from 15 different chemical groups were assayed. The results of Table 4 show that most of pesticides tested did not interfere considerably at concentrations higher than 10 ng mL^{-1}, which demonstrated the good selectivity of the proposed method with regard to other pesticides, bearing in mind that the maximum permitted concentration, established by European Community for total pesticides in surface waters is 1–3 ng mL^{-1} [41].

328 Table 4**.** Study of interferences of other pesticides on 40 ng mL^{-1} methomyl PICL signal.

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330

Pesticide	Chemical group	ng mL^{-1}	Error, %
2,4-D	Phenoxyacetic	40000[a]	-4.7
Acetamiprid	Neonicotinoid	200	-2.2
Amitrole	Triazole	200	-4.0
Myclobutanil	Triazole	40000[a]	-3.8
Carbaryl	Carbamate	400	+5.1
Pirimicarb	Carbamate	40000[a]	-3.8
Cyromazine	Triazine	40000[a]	-7.3
Chloridazon	Pyridazinone	40	3.4
Diquat	Bipyridilium	40000[a]	2.1
Diuron	Phenylurea	10	-4.1
Fenamiphos	Organophosphorus	10	17.6
Fluroxypyr	Pyridine	80	-8.1
Glyphosate	Organophosphorus	40000[a]	0
Imazalil	Imidazole	20000	-5.4
MCPA	Phenoxyacetic	20	1.7
Metalaxyl	Acylalanine	40000[a]	-1.0
Metazachlor	Acetamide	40000[a]	-0.8
Quinmerac	Quinoline	80	-8.3
Ziram	Dithiocarbamate	20	-6.1

331
332 a. Maximum concentration assayed.
333

334

335

3.5.4 Validation of the method

Methomyl was the pesticide selected to study the applicability of the proposed method, since the optimization step was developed for it. Its determination was carried out in tap, mineral and spring waters. In order to remove ionic interferences, samples were passed on-line through ionic exchangers columns prepared as stated in the experimental section. Standards were also passed through the columns containing the exchangers in order to avoid any potential change in the flow rates.

The good recoveries achieved, between 80 and 111%, (Table 5), demonstrated that the developed method could be successfully applied to the determination of methomyl in natural waters.

Table 5. Recoveries, %, obtained in the analysis of waters.

Methomyl added, ng mL^{-1}	Mineral water	Tap water	Spring water 1	Spring water 2	Spring water 3
5	106	94	80	94	111
10	101	82	87	101	100
20	93	94	97	95	96
30	90	92	102	97	90
40	99	89	96	100	85
Mean recovery±SD	98±6	90±5	92±9	97±3	97±10

4. Conclusions

A new FI-PICL method has been developed for the determination of *N*-methylcarbamates. It was based on the oxidation of these pesticides, previously irradiated with a UV lamp. Ionic interferences were removed on-line using ion-exchange resins and a low interfering effect was observed for pesticides from 15 different chemical groups. The determination of methomyl in waters was successfully carried out with mean recoveries higher

than 90%. The high sensitivity, throughputs and automation provided by CL detection and FI methodology are especially suitable for routine analysis. All these analytical features make the proposed method an interesting alternative for the screening of *N*-methylcarbamates in environmental samples.

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