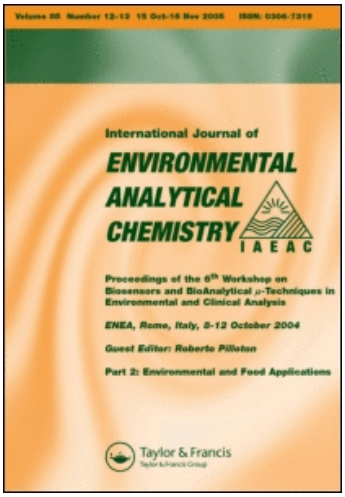

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Flow amperometric determination of carbofuran and fenobucarb

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Flow amperometric determination of carbofuran and fenobucarb

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A simple, rapid, and precise amperometric method for quantification of *N*-methylcarbamate pesticides in water samples and phytopharmaceuticals is presented. Carbofuran and fenobucarb are the target analytes. The method is developed in flow conditions providing the anodic oxidation of phenolic-based compounds formed after alkaline hydrolysis. Optimization of instrumental and chemical variables is presented. Under the optimal conditions, the amperometric signal is linear for carbofuran and fenobucarb concentrations over the range of 1.0×10^{-7} to 1.0×10^{-5} mol L^{-1}, with a detection limit of about 2 ng mL^{-1}. The amperometric method is successfully applied to the analysis of spiked environmental waters and commercial formulations. The proposed method allows 90 samples to be analysed per hour, using 500 μL of sample, and producing wastewaters of low toxicity. The proposed method permits determinations at the μg L^{-1} level and offers advantages of simplicity, accuracy, precision, and applicability to coloured and turbid samples, and automation feasibility.

Keywords: Amperometry; Carbofuran; Fenobucarb; Pesticides; Flow-injection analysis

1. Introduction

N-Methylcarbamates are pesticides of anticholinesterase activity that are responsible for toxicological effects on the nervous system of insects. However, this neurotoxicity affects most living organisms, including humans [1]. Many of these insecticides are also suspected as being carcinogens and mutagens. Their analytical control is therefore important to prevent environmental alterations upon biodiversity and to establish their persistence. The routine control on phytopharmaceuticals is also important to avoid overdose applications that would result in unnecessary overexposure for the operator and other living organisms.

Two *N*-methylcarbamates widely used are carbofuran (CB) and fenobucarb (FB). CB is the 2,3-dihydro-2,2-dimethylbenzofuran-7-yl-methylcarbamate, and FB is the

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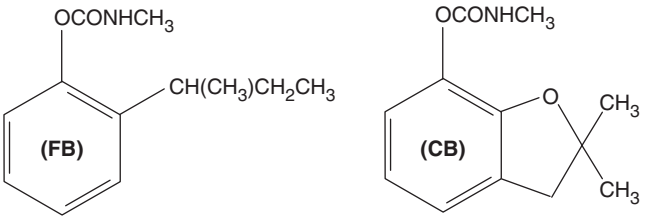

Figure 1. Chemical structure of fenobucarb (FB) and carbofuran (CB).

2-*sec*-buthylphenyl methylcarbamate (figure 1). A host of methods have been developed in the last few years for their determination. Most of these are based on instrumental separation such as gas or liquid chromatography. Classic gas-chromatographic methods are not satisfactory for carbamates because these pesticides have a tendency to break down to the corresponding phenol on the column under normal analytical conditions. Thus, this technique has been employed after derivatization steps with different reagents or columns to obtain temperature-resistant compounds [2, 3]. Sometimes alkaline hydrolysis is a first step in the derivatization to a fluorescent product [4, 5] or is the method to obtain a compound readily oxidizable (phenol derivative), and electrochemically detectable [6, 7]. High-performance liquid chromatography (HPLC) with different detectors, namely UV [8], photodiode-array [9, 10], electrochemistry [11, 12], and mass-spectrometric detection [13], is widely used in a variety of media generally involving a trace enrichment step in order to increase the sensitivity. Recently, a liquid chromatography eletrospray ionization tandem mass spectrometry (LC/ESI/MS-MS) method was developed to quantify some carbamates [14].

Other non-chromatographic approaches are also described in the literature for determination of several *N*-methyl carbamates in different matrices. These are UV/visible [15] and chemiluminescence [1, 16, 17] procedures, and enzymatic methods based on immunoassay [18–21] or biosensors [22, 23]. These are used sometimes in combination with flow-injection (FI) techniques [1, 15–17].

Still, a fast and reliable method with low detection limits for routine determinations of an *N*-methylcarbamate compound in environmental samples would be useful. The present study proposes for this purpose the development of an FI analysis (FIA) method of amperometric detection. Prior to detection, analytes are hydrolysed into their phenolic derivatives to determine an improved sensitivity. A strategy enabling alkaline hydrolysis in flow media is attempted, to provide decreased operator intervention and more efficient sampling rates *versus* reagent consumption.

2. Experimental

2.1 *Reagents and solutions*

All reagents used were of analytical grade. CB and FB were purchased from Sigma Aldrich (Spain), and others were from Merck (Portugal). The water used to prepare solutions was purified with a Milli-Q Millipore system.

Stock solutions of each pesticide (2.5×10^{-4} mol L^{-1}) were prepared in water. The corresponding solid was previously dissolved in the lowest quantity of

N,*N*-dimethylformamide (DMF). The resulting solution was kept in the dark and in a refrigerator at +4°C. More diluted standards were prepared by suitable dilution in ultra-pure water.

Acetate buffer solutions, pH 3.4–5.9, were used as supporting electrolytes and were prepared by mixing different volumes of acetic acid and sodium acetate solutions of equal concentrations until the desired pH was reached. A subsequent dilution was performed to produce solutions with an ionic strength of 0.02 mol L^{-1}. The selected buffer was of pH 5 and prepared by diluting 100.0 mL of sodium acetate 0.2 mol L^{-1} and 55.0 mL of acetic acid 0.2 mol L^{-1} up to 1.0 L.

Organic solvents required for the comparison method were of analytical grade. Before use, they were filtered, and any dissolved air was removed by bubbling nitrogen through the solution.

Tap water for analysis was provided from the laboratory tap and was collected after allowing the water to run for 1 min. The environmental water was colleted from a farm at different points separated 50 m of its path in nature. After collection, all water samples were kept in dark bottles inside the refrigerator. A formulation under the commercial name of Perfuran was obtained from a local drug company and contained CB as the active compound with a labelled amount of 5%.

2.2 *Apparatus*

The FI assembly was composed of a Gilson (France) Minipuls 3 peristaltic pump equipped with pump tubing of the same brand. Samples and standards were introduced into the carrier stream through a six-port Rheodyne®, type 5020 injection valve of exchangeable injection volumes. Omnifit (Rockville NY, USA) PTFE tubes (0.8 mm i.d.) connected by Gilson® end-fittings and joints were used in the construction of the manifold. Confluence points were made in Perspex® and were as described elsewhere [24].

Amperometric detection was carried out in a Metrohm 656 wall-jet cell (Herisan, Switzerland). Working, reference, and auxiliary electrodes were made of glassy carbon (Metrohm 6.0805.01), Ag/AgCl (KCl 3.00 mol L^{-1}, Metrohm 6.0727.000), and gold (Metrohm 6.530.320), respectively. A Metrohm 641 VA-detector was used as amperometric detector, and its output signals were recorded in a Kipp & Zonnen BD 111 strip chart recorder (Delft, The Netherlands).

When required, the glassy carbon electrode was cleaned mechanically by polishing its surface with a special kit (Metrohm 6.2802.010) with α-Al_2O_3 (0.3 μm). Before use, the electrode was washed with water and dried on tissue paper. HPLC determinations were performed with a Sykan A 1210 liquid chromatograph equipped with a model 3200 UV detector turned to 197 and 194 nm for CB and FB, respectively. Separation of sample components was accomplished on a Supercosil LC-18 column (250 mm × 4.6 mm, 5 μm particle size) from Macherey-Nagel, Germany.

The pH was measured by means of a Metrohm 632 pH meter connected to a combined glass electrode (Metrohm 6.020.000).

2.3 *Comparison method*

Results from amperometric analysis were compared with those obtained using an independent method employed by Riedel-deHaën for quality control of pro-analysis

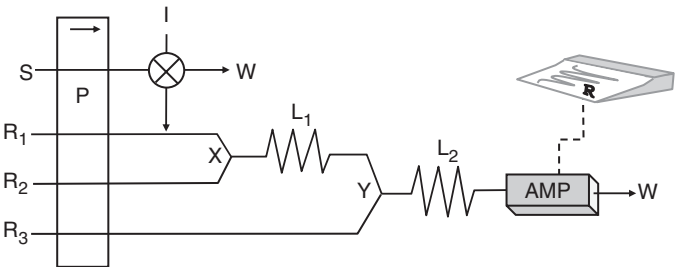

Figure 2. Flow-injection system with amperometric detection: P: peristaltic pump; S: sample; I: injection point; R_1: water; R_2: sodium hydroxide solution; R_3: acetate buffer solution; X and Y: confluence points; L_1 and L_2: coiled reactors; AMP: amperometric detector; R: recorder; W: waste. The total flow rate is $2.0\,mL\,min^{-1}$.

grade reagent [25]. HPLC was performed at room temperature with a mixture of water and acetonitrile as mobile phase at a flow rate of $1.4\,mL\,min^{-1}$. The composition was 60% water and 40% acetonitrile for CB and 50% of each component for FB. Calibration was performed after injection of 20 μL of a series of CB or FB standards with concentrations ranging from 1.0×10^{-6} to $8.0 \times 10^{-6}\,mol\,L^{-1}$.

2.4 *Flow-injection manifold and procedures*

The diagram of the flow assembly is shown in figure 2. Standard or sample solutions were injected into a deionized water carrier stream (R_1) merging in confluence X with the NaOH solution stream (R_2). In reaction coil L_1, pesticides were hydrolysed to their phenol derivatives. The sample stream then travelled to confluence Y, where the buffer acetate solution (R_3) was added. Reactor coil L_2 provided a convenient mixture between solutions of confluent channels to ensure a suitable ionic strength and pH adjustments while crossing the detection device. The increase in current was monitored using a glassy carbon working electrode *versus* an Ag/AgCl reference electrode, and with a gold electrode as auxiliary. The working electrode was mechanically polished at the beginning of the morning and afternoon evaluations. The signal output was recorded on a strip-chart recorder. FI signals were evaluated in terms of peak height, and converted in current (μA).

2.5 *Analytical procedure*

Water samples were spiked with standard solutions of CB or FB, to obtain concentration levels ranging from 1.00×10^{-6} to $3.00 \times 10^{-6}\,mol\,L^{-1}$. These values correspond to 221–664 ng of CB mL^{-1} and 207–622 ng of FB mL^{-1}. An analysis was performed by direct reading of diluted samples, and concentrations were calculated by means of the previous calibration procedure.

A representative sample of the only commercial formulation available that corresponded to an amount of CB equivalent to 25 mg was dissolved with a small volume of DMF and transferred into a volumetric flask of 50 mL. Ultra-pure water was used to make up the final volume. A second dilution was required to provide

concentration levels of about 1.0×10^{-6} and 2.0×10^{-6} mol L^{-1}. These dilutes samples were analysed after the standard addition method.

3. Results and discussion

3.1 *Preliminary studies of flow alkaline hydrolysis*

N-Methylcarbamates are carbamic esters that hydrolyse in alkaline media producing the corresponding acidic and alcohol derivatives. While the carbamate substrate presents no electrochemical activity, its alkaline hydrolysis yields a phenol derivative that is easily oxidized. The chemistry of this process is represented in figure 3.

Adaptation of this alkaline hydrolysis to flow measurements required prior evaluation of two main parameters: (1) the time given for a reaction to occur and (2) the concentration of sodium hydroxide. A potential of +0.7 V for amperometric detection was selected at this point. Previous voltammetric studies indicated maximum currents at this potential for a glassy carbon electrode [6, 7]. The flow rate was kept at 2 mL min^{-1}.

For studying the effect of time, pesticide solutions of sodium hydroxide were added before injection into the flow stream of a manifold similar to that in figure 2, with its first confluence point and reaction coil removed. For a concentration of 1.0×10^{-5} mol L^{-1} in CB or FB and 0.02 mol L^{-1} in sodium hydroxide, the time given for the reaction to occur ranged from 2 to 25 min. After injecting 200 μL of the reaction mixture, and stopping the sample plug by the detection device, 95% of maximum currents were reached in 5 min. This is a short period of time for flow measurements where readings are made long before the equilibrium is reached. Thus, the alkaline hydrolysis of pesticides may be carried out in flow media.

Keeping the pesticide level in solution, the sodium hydroxide concentration was varied from 1.0×10^{-2} to 6.0×10^{-2} mol L^{-1}. It was observed that an increase in sodium hydroxide concentration up to 4.0×10^{-2} mol L^{-1} increased the analytical signal (figure 4). Higher concentrations were conducted at lower currents, which could result from an increase in pH at the detection point due to the unsuitable buffer capacity of solution in channel R_3 (figure 2). A solution of 4.0×10^{-2} mol L^{-1} in sodium hydroxide was selected for channel R_2 in further studies.

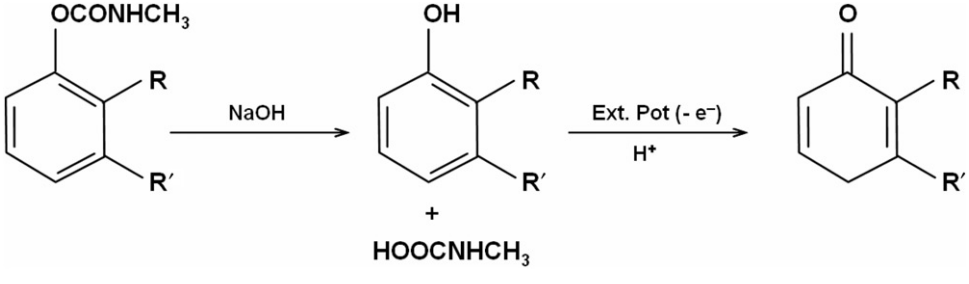

Figure 3. Alkaline hydrolysis of carbamates and its oxidation after application of suitable external potential in acidic media.

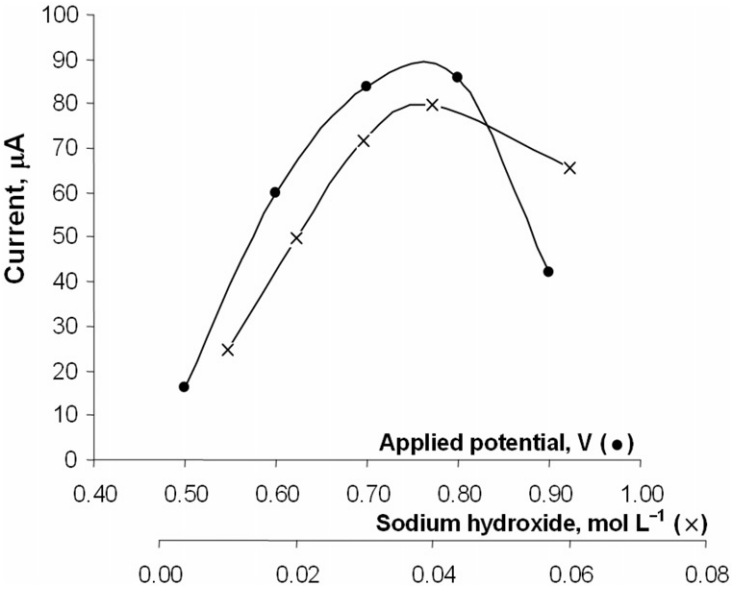

Figure 4. Effect of main chemical and amperometric variables in the analytical signal.

Table 1. Selected conditions for the flow injection amperometric system following optimization procedures

Parameter	Condition	Studied range	Selected
Chemical variables	NaOH concentration (mol L^{-1})	$(1.0–6.0) \times 10^{-2}$	4.0×10^{-2}
	pH of buffer solution	3.6–5.9	5.0
Hydrodynamic variables	Flow rate (mL min^{-1})	1.0–2.5	2.0
	Injection volume (µL)	200–1000	500
	Length of coil L_1 (cm)	0.5–1.0	75
	Length of coil L_1 (cm)	0.5–1.0	75
Amperometric analyser	Working electrode	–	Glassy carbon (3 mm Ø)
	Electrode potential (V)	0.5–09	+0.7 V (*vs.* Ag/AgCl, 3 mol L^{-1} KCl)
	Sensitivity (µA V^{-1})	–	10
	Measurement mode	–	Time base

3.2 *Optimization of the hydrodynamic variables*

The main hydrodynamic features of the flow set-up were optimized to enable sensitive and reproducible determinations of CB or FB with a high sampling throughput and without requiring manifold reconfiguration. Selection of optimum conditions followed univariant procedures.

Phenol derivatives were formed in reactor L_1 where the reaction between pesticide and sodium hydroxide solution took place. The extent of reaction was mainly governed by the length of the coiled tubing. Thus, experiments were carried out with 0.5–1.0-m reactors. A 75-cm coiled reactor was chosen for CB and FB evaluations (table 1). Smaller reactors had a decreased sensitivity and reproducibility due, presumably, to insufficient mixing of the sample with the NaOH solution (figure 5). Longer reactors

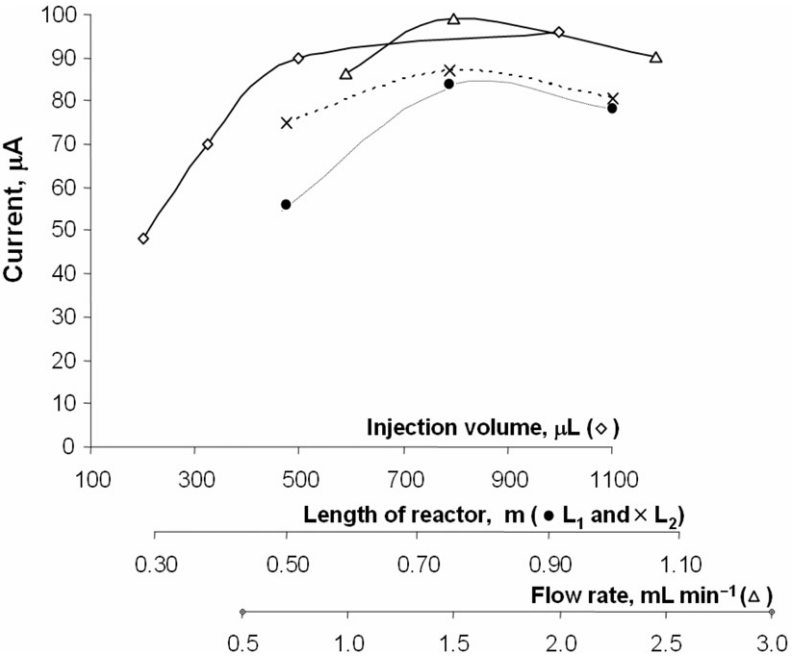

Figure 5. Optimization of hydrodynamic variables.

had a decreased sensivity and sampling rate due to the dispersion effect. The length of the reactor, L_2, was studied within the same range, and the behaviour observed was similar to that of reactor L_1 (figure 5). The use of a 75-cm L_2 coil (table 1) ensured the best compromise between sensivity and reproducibility.

The injection volume was varied between 200 and 1000 μL (table 1). The amperometric signal increased with sampling volume (figure 5), suggesting a higher sensitivity for higher injection volumes. However, the time required per analytical reading increased also because the cell-washout process took a longer time. In addition, consumption of the sample also increased. As a compromise, a volume of 500 μL was used for both analytes in the following experiments.

The overall flow rate was varied from 1.0 to 2.5 mL min^{-1} (table 1). This interval considered limitations of flow pressure exerted upon the wall-jet cell [26], with a dead volume of about 1 μL. Flow rates higher than 2.5 mL min^{-1} were not satisfactory, since they produced irreproducible signals as a result of the high pressure exerted by flowing solutions. Lower flow rates gave reproducible signals, but they compromised the sampling rate. As a compromise, results indicated the selection of a 2.0 mL min^{-1} flow rate (figure 5).

3.3 *Effect of pH*

The influence of pH in the analytical device was studied using different acetate buffer solutions, pH 3.4–5.9, as a support electrolyte. Selection of an acidic region is in agreement with previous reports for oxidation of phenols. The best sensitivity for both

pesticides was obtained with an acetate buffer of pH 5.0. This buffer was therefore selected for the determination of the phenolic derivative through the detection device.

3.4 *Effect of applied potential*

Current intensities of 1.0×10^{-5} mol L^{-1} standard solutions were measured for potentials ranging from 0.5 to 0.9 V. Similar i_p values and peak shapes were recorded for both analytes. Maximum responses were obtained for +0.7 and 0.8 V. The concomitant increase in the baseline was very small, indicating that no background oxidation occurred at these potentials. The results obtained for CB are shown in figure 4.

The detection potential of +0.7 V *versus* Ag/AgCl (3 mol L^{-1} KCl) was chosen as the optimum (table 1). Higher potentials would induce interfering effects of coexisting compounds and/or lower analytical signals.

3.5 *Fouling of working electrode*

Solid electrodes are subject to possible surface poisoning due to adsorption problems and a lack of renewable surface. This is particularly evident in the analysis of pesticides, due to the lipophilicity of the analyte itself and of its product from the electrochemical reaction. This effect is however minimized when they are used in flow systems. The continuous passage of the carrier stream helps in cleaning the electrode surface. This, in turn, saves time because electrode pre-treatment stages may be omitted. In the present study, the electrode was polished only at the beginning of each working period.

For consecutive injections of standard CB or FB solutions, a relative standard deviation was always below 1.7% (figure 6, $n = 7$). Well-defined and sharp peaks were observed with no apparent carryover (figure 6(ii)). Very short times for the washout operation are therefore implicated.

3.6 *Analytical features*

Table 2 shows the main features from calibration plots obtained under selected experimental conditions. The amperometric response showed a linear behaviour for a series of CB and FB standard solutions ranging from 1.0×10^{-7} to 1.0×10^{-5} mol L^{-1}. Limits of detection were calculated according to IUPAC recommendations [27], from the 3 s_b/m criterion, where m is the slope of the corresponding calibration graph and s_b was estimated after several readings ($n = 15$) of an amplified baseline reading.

FB calibrations showed a higher slope than those from the CB pesticide (table 2). This could be a result of substrate stabilization provided by electron delocalization from the oxygen atom bonded to the aromatic ring. This additional resonance would contribute to a decrease in reactivity conducting to lower yields from alkaline hydrolysis. No other significant differences were found between the main analytical features for both pesticides. The detection limits are about 2 ng mL^{-1} (table 2). The number of readings per hour was about 85 when standard solutions were injected.

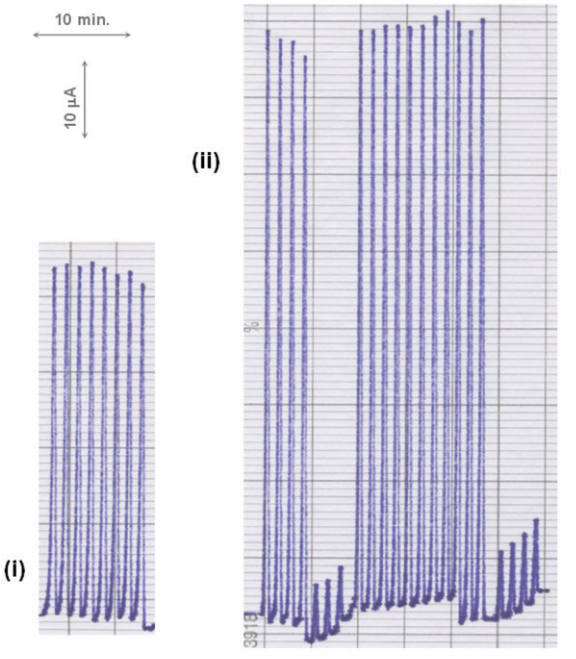

Figure 6. Repeatability of analytical signal of CB for (i) 1.0×10^{-5} and (ii) 3.0×10^{-5} mol L^{-1} with intermittent injections of 3.0×10^{-6} mol L^{-1} of pesticide.

Table 2. Main analytical features of the proposed amperometric system.[a]

	Flow-injection amperometry	
Parameter	CB	FB
Linear dynamic range (mol L^{-1})	1.0×10^{-7} to 1.0×10^{-5}	1.5×10^{-7} to 1.0×10^{-5}
Detection limit (mol L^{-1})	1×10^{-8}	1×10^{-8}
Detection limit (ng mL^{-1})	2.21	2.07
Correlation coefficient	> 0.994	> 0.996
Slope (μA mol L^{-1})	1.29×10^{5} ($\pm 1.28 \times 10^{4}$)	1.89×10^{6} ($\pm 2.65 \times 10^{4}$)
Intercept (μA)	0.139 ± 0.035	0.276 ($\pm$0.037)
Repeatability (%)	$\pm$1.62	$\pm$1.73
Sampling rate (samples h^{-1})	87	84

[a]Number of measurements: 5 for general analytical features and 7 for repeatability.

3.7 *Effect of coexisting species*

Drinking-water is expected to show simple chemical composition. With regard to Portuguese legislation [28], the maximum recommended values for chloride, sulfate, sodium, and potassium are below 25 mg L^{-1}. The recommended levels for magnesium and calcium are below 30 and 100 mg L^{-1}. Regarding unwanted substances, those with higher admissible levels are phosphorus (5000 mg L^{-1}), fluoride (1500–700 mg L^{-1}), nitrate and manganese (50 mg L^{-1}), and iron (200 mg L^{-1}). Other foreign species

are expected only at trace levels. The matrix effect of tap water upon the amperometric signals was studied by replacing the deionized water carrier by this sample. As expected, no interfering effect from sample matrix was recorded: the current of the baseline showed only a slight drift. The high electrolyte charge continuously crossing the detector already produced high background currents to enable interfering effects from ionized species in drinking-water samples.

The interference effect from the sample matrix of environmental water samples was tested similarly. Again, a slight drift of baseline occurred, but the magnitude of current alteration was negligible.

3.8 *Applications*

As representative water samples, tap and mineral waters were selected. Neither of the pesticides was detected in these waters, as expected, since pesticides are restricted in tap water, and mineral waters came from a farm where no pesticides had previously been applied. Therefore, to evaluate the suitability of this method for analysis of contaminated waters, samples were fortified at different levels. An amperometric analysis was carried out after injecting these spiked waters into the system without any prior treatment. The concentrations of pesticides in water samples were calculated from preceding calibration procedures. Commercial formulations were analysed after the standard addition method to minimize any possible matrix effects.

The mean results and corresponding standard deviations for FB and CB determinations are given in table 3. These results were compared with those provided by the comparison method by means of Student's t test and the F statistical test. A statistical comparison of these methods considered a paired two-tail test for a 5% level of significance and considered as a null hypothesis that the two methods agree. For FB and CB, the calculated t values were 0.99 and 0.59, respectively. Tabulated t values were 2.23 and 2.18, respectively, thus confirming the null hypothesis.

Table 3. Results obtained from determinations of CB and FB by using the FIA system and comparative HPLC method, showing relative errors and F values

Sample	Pesticide	Added ($\times 10^{-6}$ mol L^{-1})	Found ($\times 10^{-6}$ mol L^{-1}) FIA[a]	Found ($\times 10^{-6}$ mol L^{-1}) HPLC[a]	RE (%)	F value
Tap water	CB	1	0.99 ± 0.03	1.02 ± 0.04	−2.9	1.9
		2	2.13 ± 0.04	2.04 ± 0.05	4.6	3
		3	3.27 ± 0.02	3.18 ± 0.03	3.1	3.7
	FB	1	1.07 ± 0.02	1.04 ± 0.03	3.1	3.6
		2	2.06 ± 0.03	1.96 ± 0.04	4.8	3.5
		3	2.97 ± 0.05	3.07 ± 0.06	−3.2	1.5
Environmental water	CB	1	1.04 ± 0.04	1.00 ± 0.07	3.3	6.2
		2	1.99 ± 0.03	2.03 ± 0.04	−1.9	3.1
		3	3.01 ± 0.03	3.05 ± 0.04	−1.2	4.7
	FB	1	0.99 ± 0.03	1.02 ± 0.04	−2.4	2.4
		2	2.32 ± 0.06	2.28 ± 0.08	1.4	3.6
		3	3.02 ± 0.03	3.05 ± 0.04	−1.1	2.8
Formulation	CB	–	1.04 ± 0.05	1.01 ± 0.05	2.4	2.1
		–	2.05 ± 0.03	2.10 ± 0.04	−2.3	4.9

[a]Mean and SD of five and three determinations by FIA and HPLC methods, respectively.

The calculated F values are also below the critical value, $F(0.025(4,2) = 10.6$. This means that the results from the amperometric method are of a comparable precision to those of the comparison method, and there is no significant difference between the mean values obtained with both methods. In addition, plotting the results of the comparison method against the proposed method gives a slope close to unit (0.9901), a small origin displacement (0.0267), and a squared correlation coefficient of 0.995.

The standard deviation of three consecutive diluted samples injected in triplicate (figure 7) was $\pm 0.03\,\mu A$, thus confirming the repeatability of the proposed method. The relative standard deviations after 10 replicate injections of spiked samples were 1.6 and 1.7% for CB and FB, respectively. The sampling rates were about 92 samples

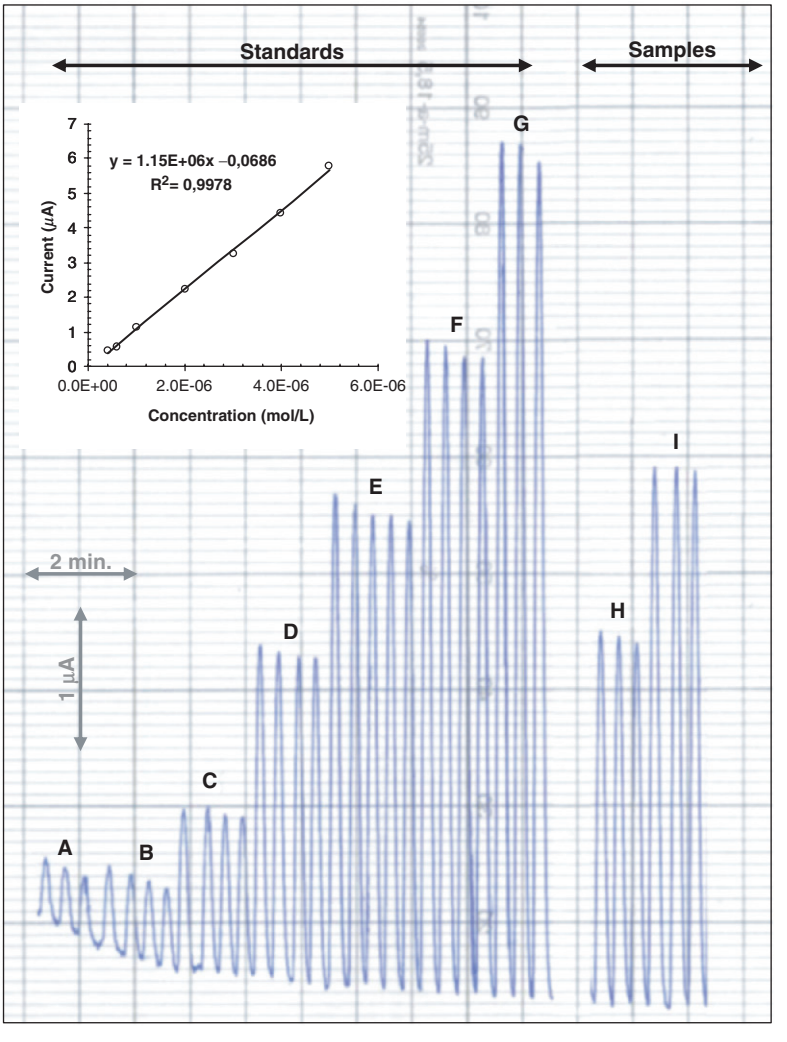

Figure 7. Flow-injection signals obtained with the amperometric system corresponding to the injection of a set of standards of CB and two spiked water samples. A: 4.0×10^{-7} mol L^{-1}; B: 6.0×10^{-7} mol L^{-1}; C: 1.0×10^{-6} mol L^{-1}; D: 2.0×10^{-6} mol L^{-1}; E: 3.0×10^{-6} mol L^{-1}; F: 4.0×10^{-6} mol L^{-1}; G: 5.0×10^{-6} mol L^{-1}; H and I, water samples. Inset: corresponding calibration curve.

per hour when real samples of $(1–3) \times 10^{-6}$ mol L^{-1} were injected. This sampling rate is slightly higher than that of the calibration procedures. This resulted from the small concentration level of pesticide in samples and suggests the absence of sample matrix effects at the electrode surface.

Regarding reagent consumption, each calibration procedure with seven standard solutions required about 10 mL of sodium hydroxide solution, 20 mL of acetate buffer, and 2 mL of each standard solution (considering four injections per standard). Moreover, several FIA records demonstrated the possibility of analysing at least five diluted samples without requiring re-calibration.

Overall, the environmental effect of the emitted effluents was considered to be of little concern, but a specific chemical treatment or selective collection/disposal could be applied if the method were to be carried out routinely. Wastewaters contain mostly acetate and a small amount of CB and FB. The expected concentration of pesticide depended on the procedure and was calculated for the experimental conditions used. Regarding the analysis of samples, and considering only the analyte, an effluent with 7.6×10^{-7} mol L^{-1} of pesticide is expected. For calibrations, effluents may contain 8.6×10^{-7} mol L^{-1}. The latter could be decreased to about 5.7×10^{-7} mol L^{-1} if calibrations were performed within 6.0×10^{-7} and 4.0×10^{-6} mol L^{-1}, within the concentration range of the analysed samples. This would promote a 33% reduction of pesticides in waste. An adjustment of pH before discarding wastewaters is necessary, as they are strongly alkaline. The total volume of effluent is also quite low, producing an average of 120 mL per hour. In terms of weight composition, effluents would contain CB within 0.17–0.19 μg mL^{-1} and FB within 0.16–0.18 μg mL^{-1}.

4. Conclusions

A simple FI amperometric system for the determination of CB and FB in natural waters and commercial formulations is described. It uses the alkaline hydrolysis of these pesticides to produce phenolic compounds that are easily oxidized on a glassy carbon surface. The method offers additional advantages associated with the FI technique such as: low reagent consumption, high throughput, and minimization of the absorption problems because the continuous passage of the carrier stream cleans the electrode surface, which in turn saves time because pre-treatment stages can be omitted. The proposed method is also precise, accurate, and inexpensive regarding reagent consumption and equipment involved. Considering its routine application, a main advantage arises from composition and quantity of emitted effluents, with a small concern in terms of environmental issues.

Globally, the method described here is a good alternative to others previously described in literature, as it offers the advantages of a fast response, long-term stability, low cost, and applicability over a wide range of concentrations and samples, with minimal sample pre-treatment and low toxicity to wastewaters.

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