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Cloud point extraction and concentration of carbaryl from natural waters

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An improved procedure is proposed for determination of the pesticide carbaryl in natural waters based on double cloud point extraction. The clean up step was carried out only with Triton X-114 in alkaline medium in order to avoid the use of toxic organic solvents as well as to minimise waste generation. Cloud point preconcentration of the product of the reaction of the analyte with *p*-aminophenol and cetyltrimethylammonium bromide was explored to increase sensitivity and improve the detection limit. Linear response was achieved within 10 and 500 $\mu\text{g L}^{-1}$ and the apparent molar absorptivity was estimated as $4.6 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The detection limit was estimated as $7 \mu\text{g L}^{-1}$ at the 99.7% confidence level and the coefficient of variation was 3.4% ($n=8$). Recoveries within 91 and 99% were estimated for carbaryl spiked water samples. The results obtained for natural water samples were in agreement with those achieved by the batch of spectrophotometric procedure at the 95% confidence level. The proposed procedure is then a simple, fast, inexpensive and greener alternative for carbaryl determination.

Keywords: cloud point; spectrophotometry; carbaryl; pesticide analysis; waters; Triton X-114

1. Introduction

The chemical analysis of environmental samples (e.g. natural waters, soils and sediments) often requires a combination of sample preparation strategies with sensitive detection techniques, usually based on expensive and sophisticated equipments [1]. An alternative is the analyte concentration and separation from the sample matrix, being the liquid–liquid extraction one of the most usual approaches [2]. The classical liquid–liquid extraction is based on the partition of the solute between two phases that form a heterogeneous system. In spite of the analytical potential, several disadvantages can be mentioned, such as the use of inflammable, toxic, carcinogenic and corrosive solvents [3]. In addition, these methods are usually laborious and time consuming, often requiring several extractions for quantitative separation [4].

An alternative to circumvent the previously mentioned drawbacks is the use of unconventional liquid–liquid extraction with surfactants. In aqueous solutions, surfactants form micelles with structures that depend on the geometry of the surfactant molecules [5]. These molecular aggregates present both hydrophilic and hydrophobic regions, which are spontaneously associated in aqueous solution from the critical micelle concentration (CMC).

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Below the CMC, surfactants are predominantly in the form of monomers in solution. In concentrations higher than the CMC, there is a dynamic equilibrium between monomers and micelles [6]. Depending on the type of surfactant, micelles can be neutral (nonionic surfactants) or charged negatively (anionic surfactants) or positively (cationic surfactants). Nonionic surfactants have a unique feature in aqueous solutions. In a given temperature and in quantities above the CMC, the separation of two isotropic phases is observed, yielding a concentrated phase containing most of surfactant and a diluted aqueous phase containing low concentration of surfactant [7]. This phenomenon, known as cloud point, allows the use of surfactants in extraction procedures, replacing the organic solvents used in conventional liquid–liquid extraction [8]. This strategy has been applied to the determination of some pesticide residues in waters [9–11].

Carbamates constitute one of the most important classes of pesticides used in agriculture. Carbaryl (1-naphthyl-*N*-methyl carbamate) has been widely used as insecticide in several crops, such as beans, bananas, potatoes, and in domestic cultures [3]. However, these compounds inhibit the cholinesterase enzyme and have a teratogenic character [12].

Several methods have been described in the literature for the analysis of carbaryl in different matrices [13–17], mainly based on chromatographic separations [18–21]. The EPA method 8318 [3], for example, is based on high-performance liquid chromatography (HPLC) with fluorimetric detection, aiming the determination of *N*-methylcarbamates in soil, water and wastes. Before the analysis, the analyte is extracted with a mixture of ethyleneglycol, methanol and acetonitrile. Spectrophotometric determination of carbaryl was also proposed [13] and implemented in flow-systems [22]. The analyte extraction was carried out with appreciable amounts of xylene followed by back-extraction, as 1-naphtholate, with 0.2 mol L^{-1} NaOH. Recently, a flow-based chemiluminescence procedure [23] was developed exploiting oxidation by Ce(IV) in a nitric acid medium containing rhodamine 6G as sensitiser. Solid-phase extraction was used to concentrate and separate the analyte from the matrix. The analyte was eluted from the cartridge with 5 mL of a 1 : 1 ethyl acetate : *n*-hexane solution. The eluent was collected and evaporated to dryness under a nitrogen stream. Ethanol was directly added to the residue and the analyte amount was then determined. A new solvent extraction and concentration procedure using microchip technology was based on thermal lens spectroscopy [24]. After pesticide hydrolysis in alkaline medium and coupling of 1-naphthol with diazotised trimethylaniline (TMA), the reaction product was extracted with toluene as a coloured azo-dye.

Other spectrophotometric procedure was based on diazotisation with TMA in a micellar medium containing sodium dodecyl sulfate [12]. The anionic surfactant was used to dissolve TMA and provides the medium where the coupling reaction with 1-naphthol was carried out. Later, the same anionic surfactant was used for acid-induced cloud point extraction coupled to derivatisation with 2-naphthylamine-1-sulfonic acid (ANSA) reagent for the determination of carbaryl residues in waters and vegetables [25].

In this work, a simple procedure for cloud point extraction and spectrophotometric determination of carbaryl in natural waters is described. The procedure is based on the alkaline hydrolysis of carbaryl to 1-naphthol which is coupled with *p*-aminophenol (PAP). After extraction of the reaction product with a nonionic surfactant, the blue species in the surfactant-rich phase is measured by spectrophotometry at 630 nm. The clean up step, often carried out with organic solvents, is replaced by a simple, fast and greener cloud point extraction.

2. Experimental

2.1 Reagents, solutions and samples

All solutions were prepared with analytical grade chemicals and distilled-deionised water. The reference solutions were prepared in the range $10.0\text{--}500.0\ \mu\text{g L}^{-1}$ (4.97×10^{-8} – $2.48 \times 10^{-6}\ \text{mol L}^{-1}$) carbaryl by dilution of a $4.97 \times 10^{-5}\ \text{mol L}^{-1}$ stock solution, prepared in 5% (v/v) ethanol. Aliquots of a $1.0\ \text{mol L}^{-1}$ sodium hydroxide solution were used for pesticide hydrolysis.

A $6.87 \times 10^{-3}\ \text{mol L}^{-1}$ PAP solution was freshly prepared by dissolving an appropriate amount of this reagent in water. A 7.5% (v/v) Triton X-114 solution was prepared in water and maintained at a temperature $<20^\circ\text{C}$. The $0.027\ \text{mol L}^{-1}$ solution of the cationic surfactant cetyltrimethylammonium bromide (CTAB) was prepared in water. A $3.5 \times 10^{-3}\ \text{mol L}^{-1}$ potassium hydroxide solution in ethanol was used to decrease the viscosity of the surfactant-rich phase, making feasible its transference to the measurement cell.

River and lake water samples were collected at Piracicaba city, São Paulo, Brazil. Samples were filtered through a $0.45\ \mu\text{m}$ cellulose acetate membrane and preserved at -4°C , being stabilised at ambient temperature immediately before analysis.

2.2 Apparatus

Absorption spectra were obtained with an UV-Vis spectrophotometer (HITACHI, Tokyo, Japan, model U-3000) equipped with a 1 cm optical path glass cell. Other spectrophotometric measurements were carried out with an UV-Vis spectrophotometer (FEMTO, São Paulo, Brazil, model 700S) equipped with reduced volume 1-cm optical path plastic cells.

The cloud point extractions were carried out in 15 mL polypropylene graduated conical tubes. A water bath at 40°C and a centrifuge (QUIMIS, São Paulo, Brazil, model Q222T) were used to induce the cloud point and accelerate the phase separation, respectively.

2.3 Sample clean up

For carbaryl extraction, aliquots of 13 mL of the sample or reference solutions containing from 10.0 to $500.0\ \mu\text{g L}^{-1}$ (4.97×10^{-8} – $2.48 \times 10^{-6}\ \text{mol L}^{-1}$) of the analyte, $400\ \mu\text{L}$ NaOH ($1\ \text{mol L}^{-1}$) and 1 mL Triton X-114 (7.5% v/v) were kept for 10 min in a thermostatic bath at 40°C . Phase separation was accomplished by centrifugation for 10 min. The aqueous phase containing carbaryl hydrolysed to 1-naphthol was then separated from the organic matter in the sample and employed for the spectrophotometric determination.

2.4 Cloud point preconcentration procedure

For the cloud point preconcentration, aliquots of 10 mL of the previously treated sample containing 1-naphthol was mixed with 1 mL PAP ($6.87 \times 10^{-3}\ \text{mol L}^{-1}$), $25\ \mu\text{L}$ CTAB (1.0% m/v) and 1 mL Triton X-114 (7.5% v/v) in graduated 15 mL tubes. The mixture was heated in a temperature-controlled water bath at 40°C for 5 min. The phase separation was accelerated by centrifuging for 5 min. The aqueous phase was removed by aspiration and the surfactant-rich phase was made up to $500\ \mu\text{L}$ with a $3.5 \times 10^{-3}\ \text{mol L}^{-1}$ potassium

hydroxide solution in ethanol, using the graduation on the tube, to decrease its viscosity. Spectrophotometric measurements were carried out at 630 nm.

2.5 Reference procedure

The batch spectrophotometric procedure adopted as reference was performed as previously described [13]. However, measurements were carried out with a multi-channel optical-fiber CCD spectrophotometer (Ocean Optics) coupled to a 100 cm optical path liquid-core waveguide flow cell (250 μL internal volume, 0.55 mm i.d.) due to the low carbaryl concentrations in the samples.

3. Results and discussion

3.1 Sample clean up and carbaryl hydrolysis

The spectrophotometric determination of carbaryl in environmental samples suffers from interferences of components in the sample matrix as well as lack of sensitivity [13–15,22,24–27]. These drawbacks have been usually circumvented by liquid–liquid extraction using organic solvents [13,22,24]. For example, one of the procedures [22] consumes 10 mL xylene per sample. In the present work, the direct carbaryl determination in natural water samples by the reaction with PAP did not provide accurate results. When samples were analysed by the proposed procedure, after addition of 200 $\mu\text{g L}^{-1}$ carbaryl, recoveries up to 216% were observed (Table 1), indicating the need of analyte separation from the organic components of the sample matrix.

It was observed that the organic matter in the samples was also extracted to the surfactant-rich phase, affecting the analyte determination. An alternative clean up procedure was then investigated in order to avoid the use of organic solvents. Carbaryl was determined after a previous extraction with 0.5% (v/v) Triton X-114 in a medium containing 0.027 mol L⁻¹ NaOH. The surfactant-rich phase retains the hydrophobic organic species that can cause interference in the spectrophotometric determination and the alkaline aqueous phase contains the hydrolysed carbaryl in the form of 1-naphthol. The efficiency of this procedure is demonstrated by comparing the absorption spectra of

Table 1. Addition-recovery experiment, mean values and estimates ($n=3$) for carbaryl determination in natural waters.

Sample	Carbaryl ($\mu\text{g L}^{-1}$)		Recovery %		
	Proposed procedure	Batch spectrophotometry [10]	Proposed procedure		Batch spectrophotometry [13] ^a
			Without clean up	With clean up	
1	186 \pm 9	196 \pm 1	98.0	93.0	98.0
2	197 \pm 4	207 \pm 12	124	98.0	103
3	181 \pm 15	181 \pm 4	179	91.0	91.0
4	198 \pm 9	214 \pm 9	216	99.2	107

Notes: Samples were spiked with 200 $\mu\text{g L}^{-1}$ carbaryl.

^aAfter sample clean up.

a spiked natural water sample with and without the clean up step with that of a reference solution containing the same carbaryl concentration (Figure 1a–c).

The extraction method was highly efficient because carbaryl is highly soluble and easily hydrolysed in the alkaline medium. This was demonstrated by a study carried out to evaluate the effect of the clean up step on carbaryl determination. When a $300 \mu\text{g L}^{-1}$ carbaryl solution was analysed in triplicate with and without the preliminary extraction, absorbance values were 0.221 ± 0.008 and 0.214 ± 0.012 , respectively. The signals did not show significant differences, indicating that the analyte remains in the aqueous phase after the cloud point extraction.

3.2 Carbaryl preconcentration

Carbaryl is hydrolysed in alkaline medium to 1-naphthol, which reacts with the oxidised form of PAP, generated by reaction with molecular oxygen or other oxidising agent. This reaction yields a highly reactive benzoquinoneimine, which reacts at the free *para* position of phenols by electrophilic attack. The formed compounds undergo rapid oxidation to yield an indophenol blue [22]. It was observed that this reaction product was completely extracted with Triton X-114. Absorption spectra (Figure 1c and d) show that the absorption maximum shifts from 608 to 630 nm after cloud point extraction of the analyte.

The effect of the parameters affecting the reaction development and micelle formation (surfactant, PAP and NaOH concentrations; temperature and incubation time and KOH concentration in the ethanol solution) were investigated in order to maximise the extraction efficiency with minimum reagent amounts and time.

The PAP concentration was the first parameter optimised, by evaluating its effect on the analytical signal for 1-naphthol determination. In the former experiments, PAP was

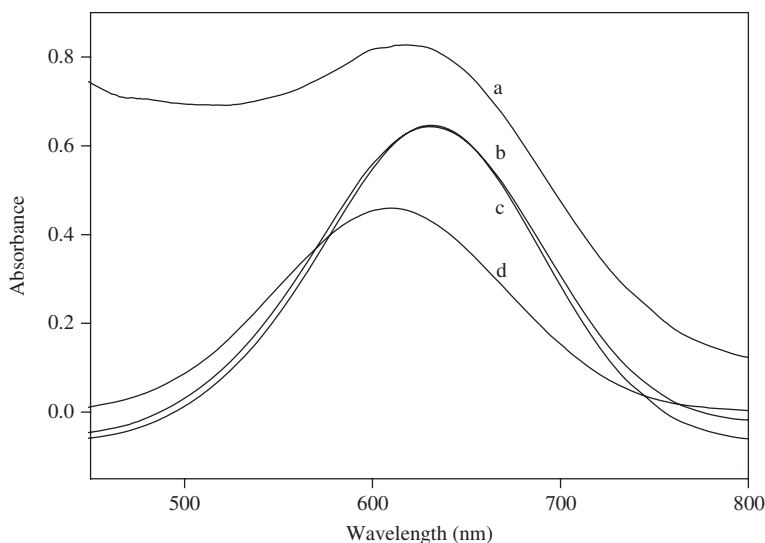


Figure 1. Absorption spectra of the cloud point extracts: (a) natural water sample spiked with $500 \mu\text{g L}^{-1}$ carbaryl without the clean up step; (b) the same spiked sample after clean up and (c) $500 \mu\text{g L}^{-1}$ carbaryl reference solution. (d) Absorption spectra of the indophenol blue (6.0 mg L^{-1} carbaryl) without cloud point extraction.

oxidised by potassium metaperiodate in alkaline medium. This study was carried out with 0.013 mol L^{-1} NaOH, $3.6 \times 10^{-4} \text{ mol L}^{-1}$ KIO_4 , 0.25% (v/v) Triton X-114 and $1.87 \times 10^{-6} \text{ mol L}^{-1}$ 1-naphthol. The PAP concentration was varied from 0.6 to $8.6 \times 10^{-4} \text{ mol L}^{-1}$, being the analytical and blank solutions subjected to the cloud point preconcentration process. The results presented in Figure 2 show that the analytical signal increases up to $5.7 \times 10^{-4} \text{ mol L}^{-1}$ PAP without significantly affecting the blank signal. Above this concentration, the blank signal increases substantially because the reagent absorbs radiation at the measurement wavelength. A $5.7 \times 10^{-4} \text{ mol L}^{-1}$ PAP concentration was then selected for further studies.

Addition of oxidising agents is usually required to convert PAP to benzoquinoneimine that reacts with 1-naphthol. Potassium metaperiodate was evaluated as oxidising agent, but sensitivity was not affected by the presence of this species, indicating that the oxygen dissolved in the solution was sufficient to act as oxidising agent. In view of these results, further measurements were carried out without addition of potassium metaperiodate.

The coupling reaction that yields the indophenol blue is favoured in alkaline medium. Concentrations within 6.7×10^{-3} and $5.3 \times 10^{-2} \text{ mol L}^{-1}$ NaOH were evaluated with $1.87 \times 10^{-6} \text{ mol L}^{-1}$ 1-naphthol and the analytical signal achieved a maximum value for $1.3 \times 10^{-2} \text{ mol L}^{-1}$ NaOH. Despite the analytical signal *ca* 10% lower, the concentration $2.7 \times 10^{-2} \text{ mol L}^{-1}$ NaOH was selected in view of the lower blank signal. In addition, sodium hydroxide is required for the conversion of carbaryl into 1-naphthol. Solutions containing the same molar concentration of 1-naphthol and carbaryl ($7.0 \times 10^{-5} \text{ mol L}^{-1}$) were treated with $2.7 \times 10^{-2} \text{ mol L}^{-1}$ NaOH, yielding analytical signals of 0.489 ± 0.002 and 0.488 ± 0.010 , respectively. In view of the quantitative conversion of carbaryl into 1-naphthol and minimisation of the blank signal in the cloud point procedure, a sodium hydroxide concentration of $2.7 \times 10^{-2} \text{ mol L}^{-1}$ was selected for further studies.

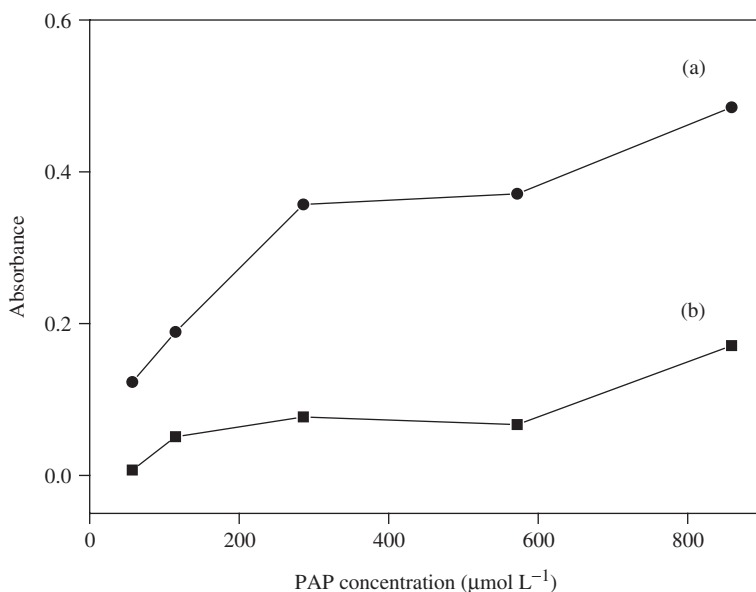


Figure 2. Effect of PAP concentration on the extraction of $1.87 \times 10^{-6} \text{ mol L}^{-1}$ 1-naphthol (a) and blank signal (b). Experimental conditions: 0.013 mol L^{-1} NaOH, $3.6 \times 10^{-4} \text{ mol L}^{-1}$ KIO_4 and 0.25% (v/v) Triton X-114.

Triton X-114 was chosen for the extraction of the reaction product in view of its convenient cloud point (23–25°C in function of the surfactant concentration) and high density of the surfactant-rich phase, which facilitates phase separation by centrifugation. The Triton X-114 concentration can affect both the extraction efficiency and the ratio between the volumes of the two phases. However, the second aspect is not relevant in the proposed experiment because the volume was ever adjusted to 500 μL before spectrophotometric measurements. Thus, the effect of the dilution of the reaction product in view of the increase of the surfactant-rich phase was not observed. In Figure 3, it can be observed that concentrations up to 0.42% (v/v) Triton X-114 were not sufficient for quantitative separation under the previously described experimental conditions. Above this concentration the analytical and blank signals were not significantly affected. The concentration of 0.60% (v/v) Triton X-114 was then chosen as optimum surfactant amount for extraction, which is 32-fold higher than the CMC ($3.5 \times 10^{-4} \text{ mol L}^{-1}$) [28] and yields *ca* 300 μL of the surfactant-rich phase after centrifugation.

In previous experiments without cloud point extraction, it was observed that the addition of CTAB increased the apparent molar absorptivity from 7514 to 10,251 $\text{L mol}^{-1} \text{ cm}^{-1}$. However, in general, the mixture of nonionic and ionic surfactants increases of the cloud point, making difficult the phase separation. For example, it was previously observed that the use of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ CTAB increases the cloud point of 1% (m/v) Triton X-114 solution from 25 to 74°C. However, this effect is significant only for concentrations above $7.5 \times 10^{-5} \text{ mol L}^{-1}$ CTAB [29]. The effect of CTAB was evaluated in the presence of $1.87 \times 10^{-6} \text{ mol L}^{-1}$ 1-naphthol. The highest sensitivity (*ca* 35% higher than that obtained without addition of CTAB) was reached with $5.48 \times 10^{-5} \text{ mol L}^{-1}$ CTAB in the extraction procedure. On the other hand, blank signals were *ca.* 2.5-times higher. Due to the increase in the blank signals, measurements were

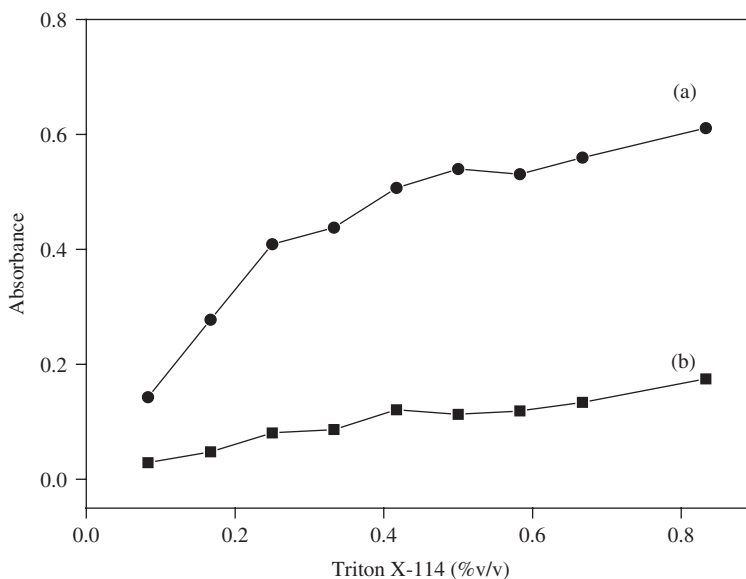


Figure 3. Variation of the analytical signal of $1.87 \mu\text{mol L}^{-1}$ 1-naphthol (a) and blank signal (b) in function of Triton X-114 concentration. Experimental conditions: 0.027 mol L^{-1} NaOH and $5.72 \times 10^{-4} \text{ mol L}^{-1}$ PAP.

carried out with addition of $3.65 \times 10^{-5} \text{ mol L}^{-1}$ CTAB, which increases the analytical signal in 15% and the blank signal in 30% in relation to the measurements without addition of the cationic surfactant. Under this experimental condition, it was evaluated that the extraction efficiency is not affected by the cationic surfactant, indicating that the increase in sensitivity is due to the higher molar absorptivity of the reaction product.

The effect of the order of reagents mixing was evaluated in different sequences, by considering both the analytical and blank signals. Variations of up to 70% were observed in the analytical signals and the best result was observed when the reagents were added in the order 1-naphthol, NaOH, CTAB and Triton X-114.

The effects of incubation and the centrifugation times were also evaluated. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which yields the complete reaction and efficient phase separation. The effects of the incubation time in a water bath at 40°C (from 5 to 20 min) and the centrifugation time in the range of 5–15 min on the extraction efficiency were investigated. These studies were carried out with $1.87 \times 10^{-6} \text{ mol L}^{-1}$ 1-naphthol, $5.72 \times 10^{-4} \text{ mol L}^{-1}$ PAP, 0.027 mol L^{-1} NaOH, $3.65 \times 10^{-5} \text{ mol L}^{-1}$ CTAB and 0.60% (v/v) Triton X-114. As both parameters did not affect critically the extraction efficiency in the ranges evaluated, incubation and centrifugation times of 5 min were defined for further studies.

Because the surfactant-rich phase presents high viscosity, ethanol was added to it after phase separation, in order to facilitate the transference to the measurement cell. However, it was observed the degradation of the indophenol blue with addition of the organic solvent in function of the pH change. Potassium hydroxide within $1.75\text{--}14.0 \times 10^{-3} \text{ mol L}^{-1}$ was added to ethanol to avoid this drawback. The best result was observed when $3.50 \times 10^{-3} \text{ mol L}^{-1}$ KOH was added to the ethanol solution. Above this concentration, the presence KOH did not affect the analytical signal but the blank signal increased up to 17%.

3.3 Analytical figures of merit

A calibration curve obtained under the optimised experimental conditions was linear over the range $10\text{--}500 \mu\text{g L}^{-1}$ carbaryl, described by the equation $A = 0.163 + 0.002 C$ ($\mu\text{g L}^{-1}$), $r = 0.999$. The detection limit was estimated as $7 \mu\text{g L}^{-1}$ at the 99.7% confidence level ($k = 3$), according to IUPAC recommendations [30], by considering the standard deviation of 8 measurements of the blank solution. The coefficient of variation ($n = 8$) was estimated as 3.4%. The enhancement factor, calculated as the ratio of the slopes of the calibration curves obtained with and without preconcentration was 29, for initial and final volumes of 15 and 0.5 mL, respectively. The extraction of the indophenol blue was then quantitative, which was confirmed by measurement of the reaction product in the aqueous phase after separation, yielding absorbance values not significantly different of the blank.

The proposed procedure was then applied to carbaryl determination in natural waters after sample spiking with $200 \mu\text{g L}^{-1}$. As showed in Table 1, recoveries within 91 and 99% were obtained by the proposed procedure, indicating absence of matrix effects. The results were also in agreement with the batch spectrophotometric procedure [13] at the 95% confidence level.

Analytical features of the proposed procedure were superior to those obtained with other spectrophotometric procedures for carbaryl determination with PAP (Table 2) [13,15,22,26,27]. The sensitivity was up to 165-fold superior to that obtained in the

Table 2. Analytical features of spectrophotometric procedures for carbaryl determination with PAP.

Procedure	Sensitivity (L mol ⁻¹)	Detection limit (µg L ⁻¹)	Coefficient of variation (%)	PAP consumption (g/1000 determination)	Ref.
Batch spectrophotometry	13,280	–	1.7, <i>n</i> = 10	0.900	[13]
FIA	4346	26	–	0.109	[22]
FIA	3521	12	0.02, <i>n</i> = 5	–	[15]
SIA	2817	26	0.14, <i>n</i> = 4	0.011	[26]
Multicommutation with solenoid-valves	4226	26	0.5, <i>n</i> = 8	0.005	[26]
Multicommutation with micropumps	10,866	51	0.76, <i>n</i> = 10	0.0028	[26]
Multicommutation with micropumps and LED photometry	4226	60	0.80, <i>n</i> = 10	0.0028	[27]
Cloud point extraction	464,806	7	3.4, <i>n</i> = 8	0.750	Proposed procedure

Note: FIA = flow injection analysis; SIA = sequential injection analysis and LED = light-emitting diode.

procedure based on sequential injection analysis [26] and the limit of detection was 8.8-fold lower than the achieved in the multicommutated flow system using solenoid micro-pumps with photometric measurements based on light-emitting diodes [27]. The detection limit is comparable with the attained by HPLC with fluorimetric detection after post column derivatisation (3 µg L⁻¹) [18], chemiluminescence (29 µg L⁻¹) [23] or thermal lens spectroscopy (14 µg L⁻¹) [24]. In addition, if necessary, sensitivity can be improved by long pathlength spectrophotometry. By employing a 100 cm optical path capillary cell (Ocean Optics), sensitivity was *ca.* 90-fold higher in comparison with the attained with a conventional 1-cm cell. Linear response was observed for carbaryl concentrations up to 4.5 µg L⁻¹, with a detection limit estimated as 200 ng L⁻¹.

The reagent consumption (0.750 mg PAP; 0.016 g NaOH and 0.200 mg CTAB for measurement) was decreased in *ca* 20% in relation to the batch spectrophotometric procedure [13]. The reagent consumption and coefficient of variation achieved in flow-based procedures were lower than in the proposed procedure, in view of the inherent characteristics of the flow systems. However, these procedures lack sensitivity and require previous separation and concentration of the analyte. These preliminary steps usually are not considered in the estimative of precision and time consumed.

The proposed procedure does not require organic solvents (e.g. xylene) for carbaryl extraction and sample clean up and presents suitable sensitivity for direct determination of the pesticide in environmental samples. The analytical features of the proposed procedure were also superior in comparison to the procedures carried out in micellar medium [12] or involving acid-induced cloud point extraction [25]. The detection limit was *ca* 30 and 7-fold lower for micellar medium and acid-induced cloud point extraction, respectively. Furthermore, these procedures require large amounts of concentrate HCl with different purposes. In procedure with TMA [12], the reagent was prepared in acid medium, also containing sodium nitrite and acetone. In procedure with ANSA [25], 5 mL of concentrate HCl was consumed for each 5 mL of sample, in order to promote cloud point phase separation.

Table 3. Relative responses for several carbamate pesticides by the proposed procedure.

Pesticide	Relative response (%)
Carbaryl	100
Aminocarb	5
Bendiocarb	5
Carbofuran	10
Pirimicarb	7
Propoxur	23

The relative response was evaluated for some carbamate pesticides (aminocarb, bendiocarb, carbofuran, pirimicarb and propoxur) from the slopes of the calibration curves obtained in the same concentration range (2.6×10^{-7} – 2.6×10^{-6} mol L⁻¹), being the results shown in Table 3. The results were in agreement with the observed in other procedures for carbaryl determination based on reaction with TMA [12] or ANSA [25]. By exploiting the reaction with PAP, it was previously observed that the formation of the indophenol blue from propoxur is slower, requiring *ca* 8 min to achieve the steady state condition, while product formation was instantaneous from carbaryl. Only propoxur showed a significant relative response, which is 5-fold lower than the achieved for carbaryl. Thus, other carbamates did not interfere significantly in carbaryl determination under the adopted experimental conditions.

4. Conclusions

The proposed procedure offers a simple, sensitive, inexpensive and greener alternative to carbaryl determination in water samples. Cloud point extraction using Triton X-114 was efficient to separate the analyte from interfering organic substances with quantitative recoveries, avoiding the use of organic solvents. The same was observed in the preconcentration step, yielding higher enrichment factors and low detection limits. In both steps, phase separation was achieved at relatively low temperatures favoring the use of the procedure for routine analysis.

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