Available online at www.sciencedirect.com
SCIENCE DIRECT
Talanta 68 (2006) 586–593
Talanta
www.elsevier.com/locate/talanta

Automatic chemiluminescence-based determination of carbaryl in various types of matrices

José Antonio Murillo Pulgarín*, Aurelia Alañón Molina, Pablo Fernández López

Department of Analytical Chemistry and Food Technology, University of Castilla La Mancha, Ciudad Real, Spain

Received 30 November 2004; received in revised form 24 April 2005; accepted 29 April 2005
Available online 24 May 2005

Abstract

Carbaryl, a modern pesticide widely used for both agricultural and non-agricultural purposes, was determined from the chemiluminescence produced in its reaction with Ce(IV) in a nitric acid medium containing rhodamine 6G as sensitizer, using flow-injection techniques. A straightforward automatic method based on measurements peak height and peak area, which are directly proportional to the carbaryl concentration, was thus developed. Calibration graphs are linear over the concentration range from 50 to 2000 ng mL^{-1}. The limit of detection, as determined according to Clayton, is 45.6 and 28.7 ng mL^{-1} for peak height and peak area measurements, respectively. The relative standard deviation for 10 samples was less than 1.4% with both types of measurements. Two commercial formulations containing carbaryl were analysed using both types of measurements, which provided acceptable recovery values. Solid-phase extraction was used to concentrate and separate the analyte from the matrix. The method was successfully applied to the analysis of spiked water samples as well as in soil and grain samples. The proposed method exhibited a high selectivity no other pesticide containing the naphthalene group such as antu, napropamide or naftalam, etc., was found to interfere with the determination of carbaryl.

Keywords: Carbaryl; Chemiluminescence; Cerium; Commercial preparations; Water; Soil; Grain

1. Introduction

The usefulness of chemiluminescent (CL) systems in analytical chemistry relies on some special features including a high sensitivity and wide dynamic ranges due resulting from their kinetic and luminescent properties, no external light source – which avoids scattering, the production of background photoluminescence, and typical problems arising from instability in external sources – reduced interference relative to non-selective processes, modest equipment requirements and a high flexibility for the determination of a wide variety of species that can participate in the CL process.

Flow-injection (FI) is by now a consolidated excellent technique for rapid, automated, quantitative analyses that combines on-line chemical and physical sample treatment with a wide range of flow-through detection systems in an enclosed, continuous flow environment. Because it allows the rapid, reproducible mixing of sample and reagent near the detector, it is particularly well suited to monitoring transient light emission from CL reactions in the liquid phase.

The FI technique has been used to investigate the fundamental chemistry of CL reactions, optimize post column reaction conditions for liquid chromatography and quantify analytes in relatively clean or synthetic matrices. In the last few years, however, there has been a marked growth in the use of FI–CL for the analysis of real sample matrices [1–12].

Also recently CL reactions have been developed by treating analytes with a wide range of strong oxidants such as MnO_4^- in acidic and alkaline media, ClO^-, Ce(IV) or H_2O_2 and reductants, under variable chemical conditions [8,13,14]. Usually, if the oxidation reaction gives a fluorescent product or the analyte itself has the typical structure for one, then one can expect its oxidation to produce CL emission. The earliest reported CL-based determinations using a flow-injection analysis assembly included those of morphine

* Corresponding author.
E-mail address: joseantonio.murillo@uclm.es (J.A.M. Pulgarín).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.04.051

[15], buprenorphine hydrochloride [16] and benzodiazepine loprazolam [17]. Since then, a variety of reactions have been used mainly for the analysis of drugs [18–21]. Sensitizers, micellar media and catalysts have been found to enhance CL emission. Thus, penicillamine [22], tiopronin [23], and cefradoxil [24] have been successfully determined in the presence of quinine sulphate; and so have folic acid [25], captopril [26], hydroclorothiazide [27], phenothiazines [28], and furosemide [29] with rhodamine 6G and hydrazine in the presence of dichlorofluoresceine [30]. Also, the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) was found to increase the sensitivity of the determination of tetracycline [31]. These reactions have been implemented mainly by use of CL-based flow-injection methods.

Modern pesticides such as *N*-methyl- and carbamoyloxime carbamates are used in large amounts for both agricultural and non-agricultural purposes. The use of non-persistent carbamate and carbamoyloxime pesticides (over 1000 t of the *N*-methylcarbamate carbaryl) – which have replaced organochlorine and organophosphorus compounds – has become a common practice as the primary result of their broad action spectrum, high effectiveness as pesticide and generally low mammalian toxicity. Their usefulness application as insecticides, fungicides, or herbicides is related to their molecular structure. Thus, the insecticides posses the *N*-substituted carbamate moiety and, generally, an aromatic ester or oxime function. Their insecticidal activity, and also their toxicity to other animals, stems from their ability to act as potent cholinesterase inhibitors.

The large amounts of carbaryl used require extensive monitoring in all types of environmental samples. A number of techniques, including chromatography [32–35], fluorimetry and phosphorimetry [36–39], have been used for this purpose. However, only four chemiluminescence-based methods have been reported. Pérez-Ruíz et al. [40] used an FI system in combination with two photochemical processes to determine carbaryl. The determination was based on the on-line photo-conversion of carbaryl into methylamine, which subsequently reacted with $Ru(bpy)_3^{3+}$ produced by off-line photo-oxidation of $Ru(bpy)_3^{2+}$ with peroxydisulphate. Orejuela and Silva [41] determined three carbamate pesticides in fruit juices by using HPLC with a peroxyoxalate CL detector. Following liquid–liquid extraction, pesticides were hydrolysed and derivatized with dansyl chloride in a micellar medium, the dansylated derivatives being separated by RP-HPLC on a C18 column and quantified from their CL signals. More recently, Huertas-Pérez et al. [42] proposed a flow-injection method for the direct determination of carbaryl, based on the enhancing effect of the pesticide on the emission produced by the oxidation of luminol with potassium permanganate in an alkaline medium. Also, *N*-methylcarbamate pesticides have been determined in environmental samples by including a fluorescent derivative of the pesticides in the peroxyoxalate chemiluminescent system, in the presence of imidazole as a catalyst [43]. The fluorescent derivate is previously obtained by decomposition of carbaryl to methylamine upon UV irradiation, followed by off-line derivatization with *o*-phthalaldehyde.

The aim of this work was to develop a simple, rapid, direct method for the determination of carbaryl, requiring no sophisticated equipment but providing results on a par with those obtained with existing methods. The proposed method is based on chemiluminescent reaction between carbaryl and Ce(IV) in an acid medium containing rhodamine 6G as sensitizer, and was successfully used to determine carbaryl in commercial formulations, water, grain and soil samples. Based on the results, the proposed method is an effective choice for the determination of this compound in various types of matrices. Also, it is simple and fast enough for use in routine analyses.

2. Experimental

2.1. Reagents

All tests were done by using with analytical reagent grade chemicals, pure solvents and Milli-Q water. Carbaryl was supplied by Chem Service.

A stock solution of carbaryl (125 mg in 1 L of ethanol) was diluted with water to prepare standard working strength solutions. The stock standard solution of carbaryl was stored at room temperature in the dark, where it remained stable for at least 2 weeks.

A 25 mM Ce(IV) solution was prepared from ammonium cerium (IV) sulphate hydrate (Panreac Química S.A., Barcelona, Spain) in 4 M nitric acid daily. A concentrated sulphuric, nitric and perchloric acid solutions were also obtained from Panreac Química S.A. Quinine hydrochloride, quinidine, riboflavin, rhodamine 6G, rhodamine B, sodium dodecyl sulphate, Triton X-100, Tween 80 and cetryltrimetylammonium bromide were purchased from Sigma–Aldrich Co. (St. Louis, MO).

The commercial technical formulation Afracid 7.5 was supplied by Afrasa Industrias (Valencia, Spain) and Agrocarbaryl from Agrofit (Valencia, Spain); the stated carbaryl content of both was 7.5.

2.2. Apparatus

The flow manifold used is depicted in Fig. 1. The reactants were propelled through its three lines by a Gilson Minipuls 3 peristaltic pump with a total flow rate of 15 mL min^{-1}. PTFE tubing (0.5 mm i.d.) was used as connectors. Aliquots of a few microliters of the sample solutions were injected into rhodamine 6G carrier via a six-way injection valve and mixed with an acid Ce(IV) solution, immediately before the PMT. The emitted CL was collected with Camspec Chemiluminiscence Detector CL-2 (photosensor module Hamamatsu No. 00 spectral response from 300 to 650 nm; spiral-type flow cell, volume 120 μl; Sawston, Cambridge). The detector was connected to a computer via an analog-to-digital converter and data were acquired using the software Cromatography

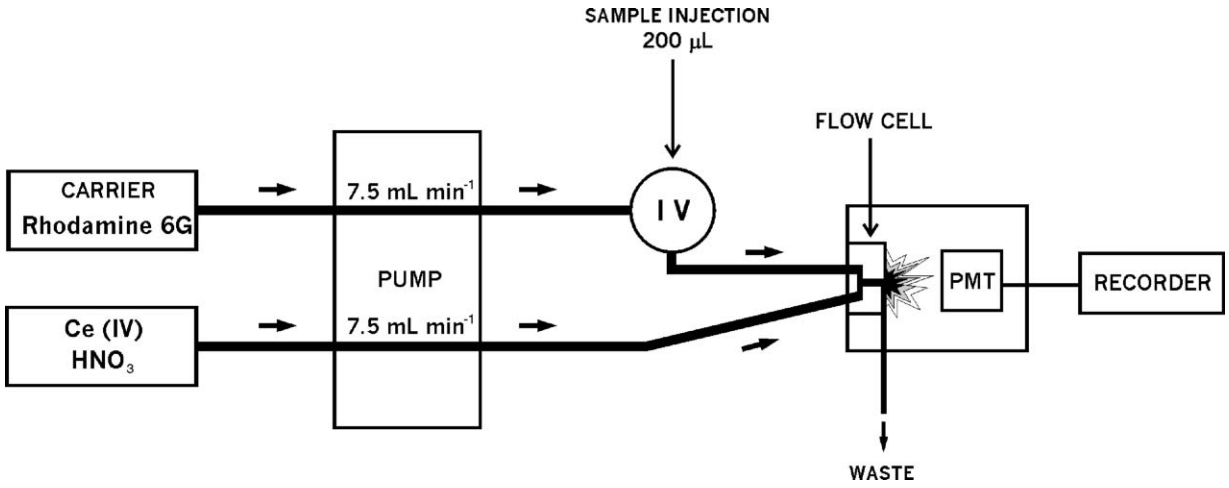

Fig. 1. Schematic diagram of the flow manifold for the determination of carbaryl.

Station for Windows CSW32 (Data Apex Ltd., Prague, The Cwech Republic) and processed by the authors.

2.3. Procedure

2.3.1. Calibration

The calibration graph was run from three replicates per point. An aliquot of the carbaryl standard solution was pipetted into a 10-mL calibrated flask at a final concentration of 50–2000 ng mL^{-1} and supplied with the volume of ethanol required to obtain a 4% (v/v) concentration. The solution was made to volume with water. The CL signal was obtained by injecting 200 μL of the working standard solution into the rhodamine 6G carrier stream, which was then merged with the acid Ce(IV) solution. The CL emission intensities and areas obtained as a function of the carbaryl concentration were used for calibration.

2.3.2. Commercial technical formulations

For the determination of carbaryl in the commercial formulations, 0.1 g of the sample was dissolved in 250 mL of ethanol, and appropriate volumes of the solution were placed in 25 mL volumetric flasks to obtain final concentrations falling within the calibration graph. The CL signal for each sample was obtained by using the general procedure on three replicates per sample; the average of each measurement was interpolated into the calibration graph.

2.3.3. Surface water samples

An aliquot of the standard aqueous solution of carbaryl (50 mg L^{-1}) was added to the surface water to obtain a concentration of 20 ng mL^{-1}.

Solid-phase cartridges packed with a reverse phase (C18 cartridges from Water Sep Pak® Vac.) were used to concentrate and separate the pesticide from its matrix. The procedure used was a modified version of that recommended by the manufacturer. The cartridge was conditioned by rinsing with 5 mL of methanol, followed by 5 mL of phosphate buffer at pH = 7. Retention and quantitative elution of the analyte from the cartridge were estimated from recovery values. A 200 mL aliquot of a 20 ng mL^{-1} solution of the analyte was added to the cartridge, which was then rinsed with 5 mL of buffer. The analyte was then eluted from the cartridge with 5 mL of a 1:1 ethyl acetate/*n*-hexane mixture. The eluent was colleted and evaporated to dryness under a nitrogen stream. The ethanol solution was directly added to the residue and the amount of analyte in the residue was then determined using the optimized method.

2.3.4. Soil and grain samples

Soil and grain samples (50 g) were spiked with an appropriate amount of carbaryl (ethanolic solution) and blended for 5 min using 150 mL of chloroform. The chloroform solution was then filtered into a 250 mL calibrated flask through Whatman No. 1 paper, the residue being retained in the blender. Blending and separation were repeated twice with 25 mL portions of chloroform. The residue was washed on the filter paper with 10 mL portions of chloroform twice, and the extracts were combined and diluted to the mark. The chloroform extract was evaporated under reduced pressure at about 50 °C and the residue dissolved with 10 mL of the ethanol solution.

3. Results and discussion

3.1. Optimization of chemical parameters

The continuous-flow manifold used to optimizate the chemical variables depicted in Fig. 2. It consisted of a peristaltic pump that propelled the sample, rhodamine 6G and acid Ce(IV) solutions through the PTFE tubes. First, the sample and rhodamine 6G solutions were merged at a Y-shaped piece and then the resulting mixture was merged with Ce(IV) in the flow cell, where the flow was abruptly stopped for measurement of the CL signal.

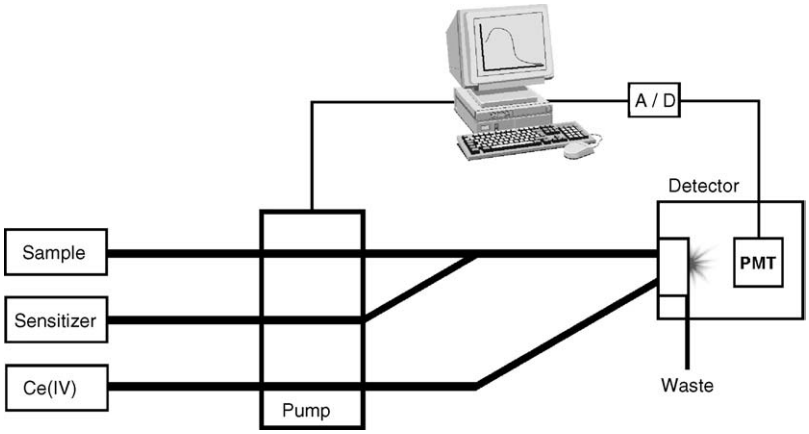

Fig. 2. Continuous-flow manifold used to the optimize of the chemical variables.

3.2. Effect of the acid added to the Ce(IV) solution

Cerium(IV) is not readily soluble in water, but is stable in dilute acid. We, thus, examined the effect of the acid added to the Ce(IV) solution. To this end, 25 mM solutions of Ce(IV) in 2 and 4 M perchloric, nitric and sulphuric acids, containing of 0.1 mM rhodamine 6G, were prepared and their light emission intensity was recorded. Nitric acid resulted in highest the CL intensity. Perchloric acid exhibited a similar sensitivity. However, no emission was detected with sulphuric acid. Therefore, nitric acid was the most suitable medium for the sensitive measurement of carbaryl.

3.3. Influence of the nitric acid concentration

The influence of the nitric acid concentration in the cerium(IV) solution on the CL intensity was examined. As shown in Fig. 3, the highest CL intensity was obtained at a nitric acid concentration of 5 M, above which the CL intensity decreased. Four molar concentration of nitric acid was adopted, in order to avoid rapid deterioration of the tubing at a higher acidity.

3.4. Effect of the Ce(IV) concentration

The effect of the concentration of Ce(IV) on the CL response of carbaryl was examined over the range 10–50 mM in 4 M nitric acid, containing 0.1 mM rhodamine 6G. The results are shown in Fig. 4. The maximum emission intensity was obtained at 25 mM Ce(IV). Higher concentrations of Ce(IV) resulted in lowering of the CL intensities. Therefore, 25 mM Ce(IV) was, thus, adopted for further testing.

3.5. Effect of sensitizers

Most CL reactions have low quantum efficiency and exhibit weak luminescence as a result. This requires adding a sensitizer, usually a highly fluorescent compound to the reaction system. Energy is transferred from the excited species to the sensitizer, which then emits its characteristic light. Because the sensitizer possesses higher quantum efficiency, it emits more photons and facilitates measurement. We examined the potencial effect of various fluorophores as sensitizers for the CL reaction. While rhodamine 6G and rhodamine B exhibited CL intensity, other compounds

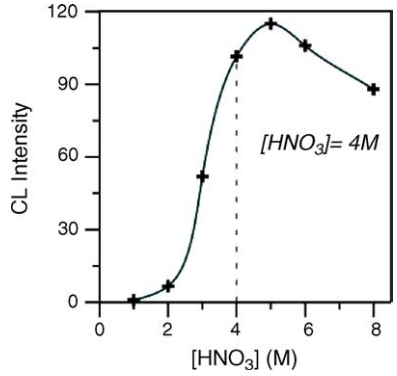

Fig. 3. Effect of the nitric acid concentration on the CL intensity.

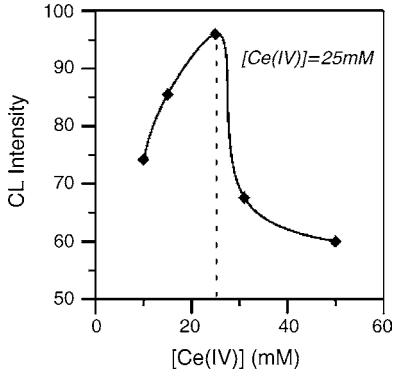

Fig. 4. Effect of the Ce(IV) concentration on the CL intensity.

such as quinine and quinidine did not because rhodamine 6G provided the highest CL efficiency; it was adopted as sensitizer for further work. The effect of its concentration was studied over the range 1×10^{-5} to 1×10^{-3} M. The CL intensity increased with increasing rhodamine 6G concentrations up to 2.5×10^{-4} M, where it levelled of and then decreased sharply above 7.5×10^{-4} M as the likely result of self-absorption of the emission by the sensitizer. Hence, a 5×10^{-4} M concentration of rhodamine 6G was used in subsequent tests. The effect of various organized systems, including neutral surfactants (Triton X-100, Tween 80), cationic surfactants (cetryltrimetylammonium bromide) and anionic surfactants (sodium dodecyl sulphate) on the CL reaction was also investigated. None was found to enhance CL emission, so no micellar solution was used.

3.6. Effect of the ethanol percentage

Because carbaryl is insoluble in water, it had to be dissolved with the aid of ethanol. The effect of the concentration of which in carbaryl solution on the CL intensity was thus studied. The CL intensity was found to decrease as the ethanol content increased. A 4% ethanol concentration was thus used, as it sufficed to dissolve carbaryl.

3.7. Optimization of FI parameters

The influence of FI variables on the chemiluminescent reaction was examined by using the above-described FI manifold (Fig. 1). The FI variables studied: the flow rate and the inserted sample volume.

3.8. Effect of the flow rate

The oxidant, sensitizer and carrier solutions were introduced into the manifold at identical flow rates. The effect of the total flow rate on the CL emission of carbaryl is illustrated in Fig. 5. Peak height increased with increasing flow rate up to 6.3 mL/min, where it levelled off and then decreased above 8.4 mL/min. Peak area increased with increasing flow rate up 4.0 mL/min and then decreased a higher values. The total flow rate selected was 6.3 mL/min.

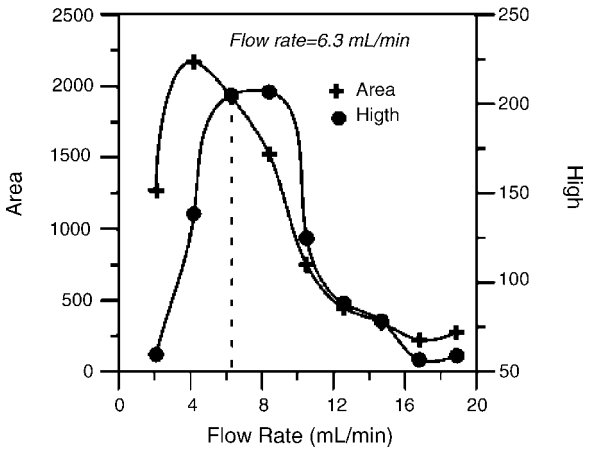

Fig. 5. Effect of the flow rate on peak height and area.

3.9. Effect of the sample volume

The variation of CL emission (peak height and area) with the injected volume was studied over the 75–300 μL range. Peak height peak increased up to 200 μL, above which it decreased. Peak area increased with increasing injected volume up to 250 μL, and then decreased slightly. An injected volume of 200 μL was adopted for subsequent testing.

3.10. Calibration curves and linearity

We used the above-described optimum conditions to develop a method for determining carbaryl over the concentration range 50–2000 ng mL^{-1}. The calibration graph was constructed from three replicates measurements per point of peak area and height. These two parameters were plotted against the carbaryl concentration and the resulting curves fitted by least-squares regression to the equation $y = a + bx$ [44,45]. Table 1 shows figures of merit of the statistical analysis. From the random residual distribution obtained, it follows that the calibration curve was homoscedastic, i.e., the variance was constant and independent of the concentration throughout the dynamic range; so both peak height and peak area were linearly related to the carbaryl concentration over the concentration range studied.

Traditional methods for determining limits of detection are biased towards protection from false positive conclusions, i.e., type I errors (reporting an analyte as present when it is not). One preferred alternative approach is to define detection limits so that protection against both false positive and false negatives (viz., type II errors, made in reporting an analyte as not present when it is) is assured. The limit of detection obtained according to Clayton et al. [46], i.e., with provision for types I and II errors, was 28.8 and 45.6 ng mL^{-1}, with peak area and peak height measurements, respectively ($\alpha = \beta = 0.05$; $n = 22$).

Table 1
Figures of merit of the statistical analysis of the carbaryl calibration

	Height method	Area method
Intercept (a)	2.93×10^{-3}	−3.30
S.D. of intercept (S_a)	0.84	4.8
Slope (b)	131.6	1187
S.D. of slope (S_b)	0.8	4.5
S.D. of regression (S_r)	2.7	15
Determination coefficient (r^2)	0.999	0.999
Confidence interval of intercept	−1.742–1.745	−13.25–6.655
Confidence interval of slope	129.9–133.3	1178–1196

3.11. Precision, accuracy and interferences—validation of the method

The repeatability of the proposed method was determined by analysing a series of 10 standard samples containing 800 ng mL^{-1} carbaryl. Application of the theory of error propagation (95% confidence level) to the calibrations graphs provided a relative standard error of 0.30% and 0.19% with peak height and peak area measurements, respectively. The respective relative standard deviations for the replicates were 1.4% and 1.3%.

The selectivity of the proposed method for carbaryl was examined by using it in the presence of other pesticides. Compounds such as chlorfenac, 2,4-dichlorophenoxyacetic acid, 2-(2,4-dichlorophenoxy)propionic acid, isoproturon, propham, diuron, neburom, linurom, napropamide, antu, naphtalam, thiobendazole, fuberidazole exhibited no interference in a proportion of 1:1. A substance was assumed to interfere when the recovery obtained in the determination of carbaryl in its presence was 95–105%.

The determination of carbaryl was validated by least-squares regression [45]. The performance of the proposed method in the determination of carbaryl in water was compared with that of a phosphorimetric method [37], by analysing 10 samples containing the pesticide at levels within the application range. The concentrations, provided by the currently accepted method and the proposed method were subjected to least-squared pair analysis. This procedure considers the effects of various types of error. The presence of random of errors in the test method causes points to scatter around the least-squares line and the calculated slope and intercept to slightly depart from unity and zero, respectively. The random error can be estimated from the standard deviation in the *y*-direction (also called the standard deviation of the estimate of *y* on *x*). A proportional systematic error leads to a change in *b*, so the difference between *b* and unity provides an estimate of the proportional error. A constant systematic error shows up in a non-zero value for the intercept. If both methods provided identical concentrations, in the same samples, then the least-squares analysis would give a zero intercept and a unit slope. Fig. 6 shows the 95% confidence region for the true slope and estimated intercept. As can be seen, the point corresponding to the zero intercept and unity slope falls within the joint confidence region, which means that the accuracy of the proposed method and the currently accepted method is not significantly different.

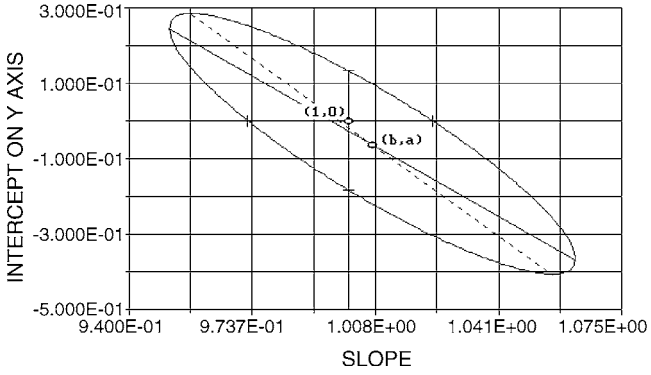

Fig. 6. Comparison of the proposed method and the phosphorimetric method. The ellipse bounds the 95% confidence region for the true slope and intercept on *y*-axis, as estimated the overall least-squares regression the concentration calculated in reverse through both. The point (b, a) is the centre of the ellipse corresponding to the true intercept and estimated slope. The point (1, 0) corresponds to a zero intercept and unity slope.

3.12. Applications

The proposed method was applied to the determination of carbaryl in two commercial products: Agrocarbaryl and Afracid 7.5. Samples were prepared, as described in Section 2. The recovery obtained with proposed method was quite consistent with nominal contents of carbaryl in the commercial preparations (Table 2) and also with those provided by the reference method [37].

The proposed method was also applied to surface water samples collected at various locations in the province of Ciudad Real (Spain). All samples were free of carbaryl or contaminated with concentrations below the detection limit. A recovery study was, therefore, carried out with standard solutions of carbaryl. The procedure was then evaluated for water samples, using the procedure described in Section 2. As can be seen from Table 2 the recoveries were quite consistent with the amounts added.

Table 2
Applications

Sample	Amount added	Recovery ± R.S.D. (%): proposed method		Recovery ± R.S.D. (%): reference method
		Height method	Area method	
Water I (ng mL^{-1})	20	95.3 ± 2.3	96.1 ± 2.6	
Water II (ng mL^{-1})	20	95.4 ± 2.1	93.2 ± 2.2	
Soil (ng g^{-1})	40	97.5 ± 2.6	98.4 ± 1.6	97.2 ± 2.1
Wheat (ng g^{-1})	40	95.3 ± 3.4	96.0 ± 1.8	96.5 ± 3.0
Barley (ng g^{-1})	40	94.5 ± 2.4	95.6 ± 2.3	96.0 ± 2.0
Oats (ng g^{-1})	40	98.1 ± 1.8	97.4 ± 2.6	98.2 ± 1.9
Afracid 7.5 (%)	7.5[a]	101.5 ± 1.5	101.4 ± 1.8	99.0 ± 1.5
Agrocarbaril (%)	7.5[a]	99.2 ± 0.8	100.4 ± 1.1	100.6 ± 2.0

R.S.D, relative standard deviation.
[a] Nominal content.

The recoveries of carbaryl from soil and grains were determined following the procedure described in Section 2. Known amounts of the insecticide were added to the samples prior to analysis. As can be seen from Table 2, the recoveries obtained with the proposed method were in excellent agreement with those of the reference method [37].

3.13. Possible CL mechanism

Based on the CL properties of the fluorophore-sensitized Ce^{IV} reaction system, examined by Zhang et al. [47], the following mechanism can be assumed for CL production by carbaryl:

$$Ce^{IV} + Carbaryl^{Red} \rightarrow Ce^{III^*} + Carbaryl^{Ox}$$

$$Ce^{III^*} \rightarrow Ce^{III} + h\upsilon$$

and/or

$$Ce^{III} - Carbaryl\ complex^* \rightarrow Ce^{III} + Carbaryl + h\upsilon$$

where Red denotes reduced form, Ox oxidized form, and (*) excited state. In the presence of a fluorophore (rhodamine 6G), the energy produced in the redox reaction can be effectively transferred to it, which, in turn, will generate the CL emission:

$$Ce^{III^*} + Rh6G \rightarrow Ce^{III} + Rh6G^*$$

or

$$Ce^{III} - Carbaryl\ complex^* + Rh6G \rightarrow Ce^{III} + Carbaryl + Rh6G^*$$

$$Rh6G^* \rightarrow Rh6G + h\upsilon$$

where Rh6G denotes rhodamine 6G.

Clearly, the fluorophore plays a central role in the energy-transfer process in our CL system, which is based on chemexcitation and the use of a key sensitizer.

4. Conclusions

The CL reaction of carbaryl with Ce(IV) in an acid medium containing rhodamine 6G is analytically useful. The proposed method is simple, rapid, fairly sensitive, selective and sufficiently accurate and precise. In addition, it requires no sophisticated instruments and the use of FI methodology to automate the overall process results in substantial timesavings. This makes the proposed method useful for the routine quality control analyses in commercial preparations.

The method provided good recoveries from spiked water samples following solid-phase extraction. The recoveries of carbaryl from soil, grain and commercial formulations testify to its usefulness analysing real samples with good selectivity.

The advantages of chemiluminescence detection are combined with those of FI methodology (e.g. good reproducibility and a high sample throughput). Other salient advantages of the proposed method include simplicity, robustness and low cost in the detector. The present method compares favourably with a previously reported CL-based method [40], involving UV irradiation of carbaryl in presence of acetone for conversion into methylamine, which entails producing $Ru(bpy)_3^{3+}$ by photochemical oxidation of $Ru(bpy)_3^{2+}$ with peroxydisulphate; this method is more complicated and uses more sophisticated instrumentation. In one other method [43], carbaryl is decomposed to methylamine and derivatized with *o*-phthalaldehyde, which results in longer analysis times among other disadvantages.

Acknowledgments

The authors gratefully acknowledge financial support from the “Dirección General de Investigación del Ministerio de Ciencia y Tecnología” and “FEDER” (Project BQ2003-03105).

References

[1] T. Hasebe, T. Kawashima, Anal. Sci. 12 (1996) 773.
[2] H. Kubo, M. Saitoh, S. Murase, T. Inomata, Y. Yoshimura, H. Nakazawa, Anal. Chim. Acta 389 (1999) 89.
[3] K.N. Andrew, M.G. Sanders, S. Forbes, P.J. Worsfold, Anal. Chim. Acta 346 (1997) 113.
[4] H.G. Beere, P. Jones, Anal. Chim. Acta 293 (1994) 237.
[5] V.A. Elrod, K.S. Johnson, K.H. Coale, Anal. Chem. 63 (1991) 893.
[6] N.P. Sen, P.A. Baddoo, S.W. Seaman, J. Chromatogr. A 673 (1994) 77.
[7] X.R. Zhang, W.R.G. Baeyens, A. Vandenborre, G. VanDerWeken, A.C. Calokerinos, S.G. Schulman, Analyst 120 (1995) 463.
[8] M.C. Sanfeliu Alonso, L. Lahuerta Zamora, J. Martínez Calatayud, Anal. Chim. Acta 437 (2001) 225.
[9] E. Nalewajko, R.B. Ramírez, A. Kojlo, J. Pharm. Biomed. Anal. 36 (1) (2004) 219.
[10] Y.Y. Sun, Y.H. Tang, X.H. Zheng, H. Yao, Z. Xu, Anal. Lett. 37 (12) (2004) 2445.
[11] B.X. Li, Z.J. Zhang, J. Wang, C.L. Xu, Talanta 61 (5) (2003) 651.
[12] P. Fletcher, K.N. Andrew, A.C. Calokerinos, S. Forbes, P.J. Worsfold, Luminescence 16 (1) (2001) 1.
[13] R.W. Abbot, A. Townshend, Anal. Proc. 23 (1986) 25.
[14] L. La Huerta Zamora, Y. Fuster Mestre, M.J. Duart Duart, G.M. Antón Fos, R. García Doménech, J. Gálvez Alvarez, J. Martínez Calatayud, Anal. Chem. 73 (2001) 4301.
[15] R.W. Abbot, A. Townshend, R. Gill, Analyst 111 (1986) 635.
[16] A.A. Alwarthan, A. Townshend, Anal. Chim. Acta 185 (1986) 329.
[17] A.R.J. Andrew, A. Townshend, Anal. Chim. Acta 26 (1989) 368.
[18] A.C. Calokerinos, N.T. Deftereos, W.R.G. Baeyens, J. Pharm. Biomed. Anal. 13 (1995) 1063.
[19] A. Roda, M. Guardigli, P. Pasini, M. Mirasoli, Anal. Bioanal. Chem. 377 (5) (2003) 826.
[20] Y. Fuster Mestre, L. La Huerta Zamora, J. Martínez Calatayud, Luminescence 16 (3) (2001) 213.
[21] P. Solich, H. Sklenarova, M. Polasek, R. Karlicek, J. Flow-Inject. Anal. 18 (1) (2001) 13.
[22] Z.D. Zhang, W.R.G. Baeyens, X.R. Zhang, G. Van der Weken, Analyst 121 (1996) 1569.
[23] Y. Zhao, W.R.G. Baeyens, X.R. Zhang, A.C. Calokerinos, K. Nakashima, G. Van der Weken, Analyst 122 (1997) 103.
[24] F.A. Aly, N.A. Alarfaffj, A.A. Alwarthan, Talanta 47 (1998) 471.
[25] A.A. Alwarthan, Anal. Sci. 10 (1994) 919.

[26] Z.D. Zhang, W.R.G. Baeyens, X.R. Zhang, G. Van der Weken, J. Pharm. Biomed. Anal. 14 (1996) 939.
[27] J. Ouyang, W.R.G. Baeyens, J. Delanghe, G. Van der Weken, A.C. Calokerinos, Talanta 46 (1998) 961.
[28] F.A. Aly, N.A. Alarfaffj, A.A. Alwarthan, Anal. Chim. Acta 358 (1998) 255.
[29] Y. Rao, X.R. Zhang, G.O. Luo, W.R.G. Baeyens, Anal. Chim. Acta 396 (1999) 273.
[30] A. Safavi, M.R. Baezzat, Anal. Chim. Acta 358 (1998) 121.
[31] Z. Li, Z.B. Wang, Xiamen Dauxue Xuebao 36 (1997) 804.
[32] D. Stajnbaher, L. Zupancic-Kralj, J. Chromatgr. A 1015 (2003) 185.
[33] M. Anastassiades, K. Mastovska, S.J. Lehotay, J. Chromatgr. A 1015 (2003) 163.
[34] M. Fernández, Y. Pico, J. Manes, Chromatgraphia 58 (2003) 151.
[35] S. Thapar, R. Bhushan, R.P. Mathur, Biomed. Chromatogr. 9 (1995) 18.
[36] L.F. Capitán-Valley, M.K.A. Deheidel, R. Avivad, Fresenius' J. Anal. Chem. 362 (1998) 307.
[37] A. Segura-Carretero, C. Cruces-Blanco, J.F. Fernández-Sánchez, B. Cañabate-Díaz, A. Fernández-Gutiérrez, J. Agric. Food Chem. 48 (2000) 4453.
[38] J.L. Vílchez-Quero, J. Rohand, R. Avivad-Castaneda, A. Navalón, L.F. Capitan-Valley, Fresenius' J. Anal. Chem. 350 (1994) 626.
[39] M. del-Olmo, J.J. Laserna, D. Romero, J. Rohand, J.L. Vílchez, Talanta 44 (1997) 443.
[40] T. Pérez-Ruíz, C. Martínez-Lozano, V. Tomás, J. Martín, Anal. Chim. Acta 476 (2003) 141.
[41] E. Orejuela, M. Silva, J. Chromatogr. A 1007 (2003) 197.
[42] J.F. Huertas-Pérez, A.M. García-Campana, L. Gámiz Gracía, A. González Casado, M. del Olmo Iruela, Anal. Chim. Acta 524 (1–2) (2004) 161.
[43] J.J. Soto-Chinchilla, A.M. García-Campana, L. Gámiz Gracia, L. Cuadros Rodríguez, J.L. Martínez Vidal, Anal. Chim. Acta 524 (1–2) (2004) 235.
[44] P.D. Lark, B.R. Craven, R.C.L. Bostworth, The Handling of Chemical Data, Pergamon Press, Exeter, 1968 (Chapter 4).
[45] D.L. Massart, B.G.M. Vandeginste, S.N. Deming, L. Kaufman, Chemometrics: A Textbook, Elsevier, Oxford, UK, 1988.
[46] C.A. Clayton, J.W. Hines, P.D. Elkins, Anal. Chem. 59 (1987) 2506.
[47] X.R. Zhang, W.R.G. Baeyens, A.C. Colokerinos, K. Imai, G. Van der Weken, Anal. Chim. Acta 303 (1995) 121.