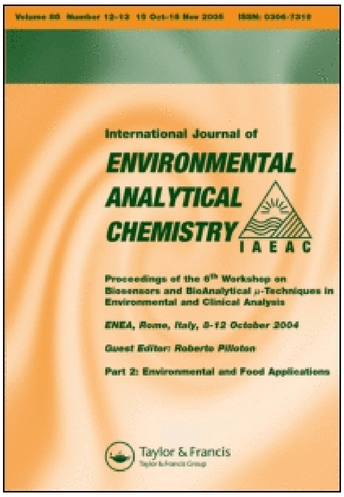

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Determination of carbaryl by flow injection with luminol chemiluminescence inhibition detection

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Determination of carbaryl by flow injection with luminol chemiluminescence inhibition detection

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A flow-injection procedure is described for the determination of carbaryl based on its inhibition effect on luminol-cobalt(II) chemiluminescence reaction in alkaline medium in the presence of hydrogen peroxide. The calibration data over the range 5.0×10^{-7} to 20×10^{-6} M give a correlation coefficient (r^2) of 0.9972 with relative standard deviations (RSD; $n = 4$) in the range of 1.0–2.1% with a limit of detection ($3 \times$ blank noise) of 2.37×10^{-7} M for carbaryl. The sample throughput was $120\,h^{-1}$. The effects of some carbamates, anions, and cations were studied on luminol CL system for carbaryl determination. The proposed method has been applied to determine carbaryl in natural waters.

Keywords: Flow-injection analysis; Chemiluminescence; Inhibition; Carbaryl

1. Introduction

Carbaryl (1-naphthyl methylcarbamate) is a wide-spectrum carbamate insecticide which controls over 100 species of insects on various crops, poultry, and livestock as well as used as a molluscicide and an acarcide [1]. It is found in all types of formulations including baits, dusts, wet table powder, granules, oil, molasses, aqueous dispersions, and suspensions [2]. Its wide use is due to its high volatility, low solubility in water, short residual life, and relatively low toxicity related to the inhibition of the enzyme cholinesterase and teratogenic potential [3].

Flow injection with chemiluminescence detection (FI-CL) has been extensively used for the determination of numerous analytes in environmental, pharmaceutical, clinical, biochemical, food, and beverage samples at low concentrations [4–6]. FI-CL methods include a high sensitivity, a wide linear dynamic range, and simple instrumentation. There are many inorganic and organic chemical reactions that produce CL in the liquid phase. However, only a few different systems have been used for analytical

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purposes including luminol, lucigenin, lophine, gallic acid, morphine, codeine, pyrogallol acridinium esters, acidic potassium permanganate, and *tris*(2,2-bipyridyl)ruthenium(II) [7–9].

Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) is one of the mostly commonly used CL reagents. The oxidation of luminol in an alkaline medium to produce the excited 3-aminophthalate anion, which emits light when it is relaxed to the ground state, with a quantum yield of 0.01 in water and 0.05 in dimethyl sulfoxide [6]. Several oxidants, like permanganate/perchlorate, periodate, hexacyanoferrate(III), and hydrogen peroxide can be used. This reaction is catalysed by metal ions such as Fe^{2+}, Cu^{2+}, Co^{2+}, and Mn^{2+}, and offers a powerful application as a detection system in FIA, LC, and CE, where luminol compounds can be used as derivative reagents that allow the analytes to be detected at very low levels [10].

Various methods have been reported for the determination of carbaryl in diverse samples. These include; spectrophotometry coupled with flow injection [11–14], fluorescence [15, 16], HPLC-UV [17, 18], GC-ECD/MS [19], and immunoassay [20]. However, some of these techniques involve expensive instrumentation, require a complicated manifold and high reagent consumption, and have low detection limits and a poor sample throughput.

Different chemiluminescence (CL) systems coupled with flow-injection (FI) manifolds or high-performance liquid chromatography and fluorimetric methods have been reported for the determination of pesticides in environmental samples and vegetal foods [21, 22]. A FI-CL method has been reported, based on the enhancing effect of carbaryl on the CL emission generated by the oxidation of luminol with potassium permanganate in an alkaline medium [23]. The limit of detection (3σ) is $4.9\,ng\,mL^{-1}$. Another direct FI-CL method has been reported, based on the CL-emission generated by the oxidation of carbaryl with potassium permanganate in acidic medium [24]. The limit of detection ($S/N = 3$) is $14.8\,ng\,mL^{-1}$ with a high reproducibility ($RSD = 2.29\%$) for $0.1\,\mu g\,mL^{-1}$ carbaryl ($n = 10$). An FI system combined with two photochemical processes has been reported for the determination of carbaryl [25]. The method is based on the on-line photo-conversion of carbaryl into methylamine, which subsequently reacts with $Ru(bpy)_3^{3+}$ generated through the on-line photo-oxidation of $Ru(bpy)_3^{2+}$ with peroxydisulfate. The limit of detection is $0.012\,\mu g\,mL^{-1}$ with a sample throughput of $200\,h^{-1}$. Soto-Chinchilla *et al.* [26] have reported an FI-CL method for the determination of carbaryl in natural waters and vegetal samples. This procedure is based on a *bis*(2,4,6-trichlorophenyl)oxalate-hydrogen peroxide reaction with previous off-line hydrolysis of the carbaryl to obtained methylamine, which is derivatized with *o*-phthalaldehyde to form fluorohpore using imidazole as a catalyst. The limit of detection is $0.031\,\mu g\,mL^{-1}$. These methods are accurate and selective but require a complicated manifold, high reagent consumption, high flow rates, and use of fluorophores and poor sample throughput. Inhibition methods using immobilized enzymes have also been reported for the determination of organophosphorus and carbamate pesticides [27–30].

This study reports an FI method for the determination of carbaryl based on its inhibition effect on luminol-cobalt(II) CL in alkaline medium in the presence of hydrogen peroxide. Manifold parameters have been optimized, and the method is applied to the determination of carbaryl in water samples. The limit of detection is 2.37×10^{-7} M carbaryl with a sample throughput of $120\,h^{-1}$.

2. Experimental

2.1 *Reagents and solutions*

All chemicals were of analytical reagent grade, supplied by Merck BDH (Poole, UK) unless stated otherwise and were used without further purification. All glassware used during the experiments and for storage of reagents and standards was pre-cleaned with 10% HCl for a week and thoroughly rinsed with ultra-high-purity (UHP) deionized water ($18.2\,\mathrm{M\Omega\,cm^{-1}}$, Elgastat-Maxima, High Wycombe, UK). Carbaryl (Dr Ehrenstorfer GmbH Laboratories) stock solution (1.0×10^{-3} M) was prepared in acetonitrile (50%, v/v) followed by sonicating for 10 min at room temperature, and subsequent standard solutions were prepared daily by serial dilution of the stock solution with UHP water. Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione; Sigma, St. Louis, MO) stock solution (0.01 M) was prepared by dissolving 0.177 g in dilute sodium hydroxide solution followed by sonicating for 30 min. A working luminol solution (5.0×10^{-6} M) was prepared by diluting the required volume in borate buffer (0.05 M, pH 11). Cobalt(II) stock solution (0.01 M) was prepared by dissolving 0.291 g of $Co(NO_3)_2$ in 100 mL of HCl solution (0.01 M), and working standard solution (1.0×10^{-6} M) was prepared daily by dilution of the stock solution with UHP water. Hydrogen peroxide solution (0.01 M) was prepared by diluting the required volume in UHP water, and a working standard solution was prepared in borate buffer (0.05 M, pH 11). Stock solutions (1.0×10^{-3} M) of carbofuran, carbophenothion, malathion, and aldicarb in acetonitrile (50%, v/v); (0.01 M) cations (Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, K^+ and NH_4^+ in HCl solution, 0.01 M) and anions (Cl^-, NO_3^-, NO_2^-, and SO_4^{2-} in UHP water) were prepared for interference studies and subsequent standard solutions of each were prepared by serial dilution of the stock solutions with UHP water.

2.2 *Instrumentation and procedure*

The flow-injection chemiluminescence manifold used for this work is shown in figure 1. A peristaltic pump (Ismatec Reglo, Switzerland) was used to deliver the sample carrier and reagent solutions at a flow rate of $1.5\,\mathrm{mL\,min^{-1}}$. A rotary injection valve

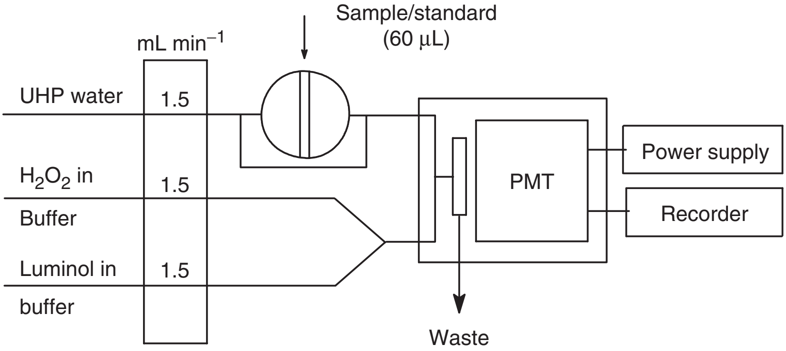

Figure 1. Flow-injection chemiluminescence manifold for the determination of carbaryl.

Table 1. Optimization of variables for the determination of carbaryl ($n = 4$).

Parameter	Range	Optimized
Borate buffer (0.05 M) (pH)	10.0–11.5	11.0
Luminol (M)	1.0×10^{-7} to 1.0×10^{-5}	5.0×10^{-6}
Cobalt(II) (M)	1.0×10^{-8} to 1.0×10^{-5}	1.0×10^{-6}
Flow rate (mL min^{-1})	0.5–2.5	1.5
Injection volume (µL)	30–180	60

(Rheodyne 5020, Anachem, Luton, UK) was used to inject carbaryl standards (60 µL) containing cobalt(II) 1.0×10^{-6} M into a UHP water stream and merged at a T-piece with luminol (5.0×10^{-6} M) and hydrogen peroxide (5.0×10^{-6} M) stream. The merged stream travelled 3.0 cm before passing through a glass spiral flow cell (1.1 mm i.d., 130 µL internal volume) placed directly in front of an end window photomultiplier tube (PMT, 9798B, Electron Tubes, Ruislip, UK). The PMT, glass coil, and T-piece were enclosed in a light, tight housing [31]. The PMT was attached to a 2 kV power supply (Burle, PF1053, Lancaster, PA). The detector output was recorded using a chart recorder (Kipp & Zonen BD 40, Holland).

3. Results and discussion

3.1 *Optimization of the FI manifold*

The experimental conditions for the inhibition of luminol-cobalt(II) CL in the presence of hydrogen peroxide by carbaryl in an alkaline medium were optimized using a univariate approach. The key parameters optimized were borate buffer pH, luminol, cobalt(II) and hydrogen peroxide concentrations, sample volume, sample carrier, and reagent flow rates (table 1). All these studies were performed with 5.0×10^{-6} M carbaryl solution containing cobalt(II) 1.0×10^{-6} M and a PMT voltage of 850 V.

The efficiency of luminol chemiluminescence is highly dependent on reaction pH. Borate/NaOH buffer pH has been reported previously to give a higher CL intensity with luminol as compared with other buffers [32]. Therefore, in the proposed FI-CL system, the effect of borate concentration was studied in the range of 0.01–0.1 M, adjusting the pH 11 with NaOH solution. However, the maximum CL inhibition with carbaryl was observed at a borate concentration of 0.05 M. The effect of borate buffer pH (0.05 M) was investigated in the range of 10–11.5, and the maximum CL inhibition was observed at pH 11. Sodium hydroxide solution of different concentrations was also investigated to check the response of luminol (5.0×10^{-6} M) for the inhibition process. The maximum CL inhibition was observed at 0.1 M sodium hydroxide, but this CL signal was lower (20%) than with borate buffer (0.05 M, pH 11). Therefore, borate buffer (0.05 M, pH 11) was selected and used for subsequent studies. The effect of luminol concentration was then studied in the range 1.0×10^{-7} to 1.0×10^{-5} M using the optimized borate buffer (0.05 M, pH 11). The maximum CL inhibition was observed at 5.0×10^{-6} M of luminol concentration and further increases resulted in non-reproducible CL signals with high blank values. Therefore, a luminol solution of

Table 2. Calibration data for carbaryl ($n = 4$).

Carbaryl (M)	Inhibition (%)[a]	RSD (%)
Blank (UHP water)	0.1	1.2
5.0×10^{-7}	10	1.0
2.5×10^{-6}	18	1.8
5.0×10^{-6}	26	2.0
10.0×10^{-6}	48	1.7
20.0×10^{-6}	95	2.1

[a] $100(CL_o - CL_t)/CL_o$, where CL_o is the peak height CL in the absence of carbaryl, and CL_t is the peak height CL in the presence of carbaryl.

5.0×10^{-6} M was selected for further studies. The CL response varied with the age of the luminol solution [33], and so it was always prepared 24 h before use. The effect of hydrogen peroxide on the determination of carbaryl was investigated in the range 1.0×10^{-7} to 5.0×10^{-5} M. There was an increase in CL inhibition up to 5.0×10^{-6} M, and a further increase in hydrogen peroxide concentration produced noisy signals. Therefore, a hydrogen peroxide solution of 5.0×10^{-6} M was used for subsequent studies. The effect of cobalt(II) concentration in the range of 1.0×10^{-8} to 1.0×10^{-5} M was studied. A maximum CL inhibition with carbaryl concentration (5.0×10^{-6} M) was observed at 1.0×10^{-6} M cobalt(II); further increases in cobalt(II) concentration levelled off the CL inhibition. Therefore, a solution of 1.0×10^{-6} M cobalt(II) was used subsequently.

The effect of key physical parameters is shown in table 1. Flow rates for each of the three channels were simultaneously investigated over the range 0.5–2.5 mL min^{-1} in terms of sensitivity, sample throughput, and reagent consumption. A flow rate of 1.5 mL min^{-1} gave the maximum CL inhibition with a steady baseline and reproducible peak height. The optimum flow rate (1.5 mL min^{-1}) depends on the distance from the T-piece to the glass coil placed in the front of PMT, which in this case is 3.0 cm [34]. Similarly, a sample injection volume of 60 µL gave almost the highest CL inhibition and was used for economy of sample consumption.

3.2 *Analytical figures of merit*

Under the optimum conditions, the calibration data of CL inhibition *versus* concentration of carbaryl over the range 5.0×10^{-7} to 20×10^{-6} M were obtained ($r^2 = 0.9972$, $n = 5$) using the regression equation $y = 21.895x + 6.1191$ (y = CL inhibition (%), x = concentration (M), carbaryl residue). The calibration data are given in table 2. The relative standard deviation (RSD) was 1.0–2.1% ($n = 4$) over the range studied, and the limit of detection (3 × blank noise) was 2.37×10^{-7} M carbaryl residue with a sample throughput of 120 h^{-1}.

3.3 *Interferences*

The effect of various species on the determination of carbaryl (2.5×10^{-6} M) containing cobalt(II) (1.0×10^{-6} M) is shown in table 3. Ca^{2+}, Mg^{2+}, Zn^{2+}, Cl^-, NO_13^-, NO_2^-, SO_4^{2-}, carbofuran, carbophenothion, malathion, and aldicorb had no significant effect

Table 3. Effect of various species on the determination of carbaryl[a] ($n = 4$).

Ions/organics	Concentration (M)	Inhibition (%)
Ca^{2+}	2.5×10^{-3}	18 ± 0.8
Mg^{2+}	8.23×10^{-4}	19 ± 1.0
Zn^{2+}	1.54×10^{-5}	15 ± 2.0
Fe^{2+}	1.78×10^{-7}	13 ± 1.6
Fe^{3+}	1.78×10^{-6}	10 ± 1.2
Cu^{2+}	1.59×10^{-6}	36 ± 1.7
K^{+}	6.4×10^{-4}	18 ± 1.9
NH_4^{+}	2.2×10^{-3}	36 ± 2.0
Cl^{-}	5.6×10^{-3}	11 ± 1.0
NO_3^{-}	4.0×10^{-4}	10 ± 1.5
NO_2^{-}	1.09×10^{-4}	35.5 ± 2.0
SO_4^{2-}	2.08×10^{-3}	15 ± 1.0
Carbofuran	4.52×10^{-6}	19 ± 1.2
Carbophenothion	2.9×10^{-6}	18 ± 1.5
Malathion	3.0×10^{-6}	16 ± 1.1
Aldicarb	5.25×10^{-6}	11 ± 2.1

[a] % inhibition of carbaryl (2.5×10^{-6} M) on luminol (5.0×10^{-6} M) – Co^{2+} (1.0×10^{-6} M) – CL system is 18 ± 1.2.

Table 4. Recovery of carbaryl residue from fortified water samples.

Type of water	Spiked (mg mL^{-1})	Found (mg mL^{-1})[a]	Recovery (%)
UHP water	0.1	0.099 ± 0.013	99
	0.5	0.491 ± 0.008	98.2
Tap water	0.1	0.095 ± 0.006	95
	0.5	0.482 ± 0.07	96.4
Lake water	0.1	0.084 ± 0.01	84
	0.5	0.433 ± 0.08	86.6

[a] Mean of six injections.

on the CL signal blank, while K^+ and NH_4^+ had a slight enhancing effect on the CL blank. Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, K^+, carbofuran, and carbophenthion had no significant inhibition effect on the carbaryl CL inhibition, while Cu^{2+}, NH_4^+, and NO_2^- had a suppressive effect on the carbaryl response. Cl^-, NO_3^+, SO_4^{2-}, malathion, and aldicarb had a slight enhancing effect on the response. The method is simple and sensitive, but the presence of these diverse ions/organics needs to be removed before it could be used for carbaryl determination in environmental samples.

3.4 *Applications*

The proposed method was applied to the recovery of carbaryl from various natural water samples by spiking experiments. Lake-water samples (from Hanna valley, Quetta) and tap-water samples (from university) were collected into acid-washed (10%, v/v HCl) high-density polyethylene (HDPE) bottles. After collection, samples were filtered through a cellulose membrane filter (cellulose acetate, pore size 0.45 µm, 47 mm diameter, Whatman, Maidstone, UK) to remove the suspended solids, kept refrigerated in the dark at 4°C. The data are shown in table 4. The recoveries are satisfactory except for lake water, possibly due to the high organic matter content of the samples (mostly humic acids) which may reduce the analytical signal due to oxidant consumption or retardation of the kinetically controlled luminescent oxidation reaction of carbaryl [24].

4. Conclusion

The proposed FI-CL method for the determination of carbaryl in water is simple and rapid ($120\,h^{-1}$ sample throughput), and the recoveries are within the acceptable range for pesticide residue analysis. The method has a detection limit of 2.37×10^{-7} M carbaryl residue.

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References

[1] J.H. Ruzicka. *Proc. Soc. Anal. Chem.*, **10**, 32 (1973).
[2] U.S. Environmental Protection Agency, Office of Drinking Water. Carbaryl Health Advisory. Draft Report, August (1987).
[3] M. Del Olmo, J. Laserna, D. Romero, J. Rohand, J.L. Vilchez. *Talanta*, **44**, 443 (1997).
[4] P. Fletcher, K.N. Andrew, A.C. Calokerinos, S. Forbes, P.J. Worsfold. *Luminescence*, **16**, 1 (2001).
[5] Y.F. Mestre, L.L. Zamora, J.M. Calatayud. *Luminescence*, **16**, 213 (2001).
[6] A.M. Garcia-Campana, W.R.G. Baeyens (Ed.). *Chemiluminescence in Analytical Chemistry*, Marcel Dekker, New York (2001).
[7] F. Fujiwara, T. Kumamaru. *Spectrochimica Acta Rev.*, **13**, 339 (1990).
[8] B.J. Hindson, N.W. Barnett. *Anal. Chim. Acta*, **445**, 1 (2001).
[9] B.A. Gorman, P.S. Francis, N.W. Barnett. *Analyst*, **131**, 616 (2006).
[10] M. Yamaguchi, H. Yoshida, H. Nohta. *J. Chromatogr. A*, **950**, 1 (2002).
[11] P. Yanez-Sedeno, C.N. Nova, L.M.P. Diez. *Microchem. J.*, **38**, 370 (1988).
[12] K.D. Khalaf, A. Morales-Rubio, M. de Ia Guardia. *Anal. Chim. Acta*, **280**, 231 (1993).
[13] L. Alvarez-Rodriguez, L. Monferrer-Pons, J.S. Esteve-Romero, C.M.C. Garcia-Alvarez, G. Ramis-Ramos. *Analyst*, **122**, 459 (1997).
[14] B. Fernadez-Band, P. Linares, M.D. Luque de Castro, M. Valcarcel. *Anal. Chem.*, **63**, 1672 (1991).
[15] A. Navas Diaz, F. Garcia Sanchez, M.M. Lopez Guerrero. *Talanta*, **60**, 629 (2003).
[16] J.R. Lakowiez. In *Topics in Flurescence Spectroscopy*, J.R. Lakowiez (Ed.), Vols 1–6, Kluwer Academic/Plenum, New York (1999).
[17] G.S. Nunes, M.L. Ribeiro, L. Polese, D. Barcelo. *J. Chromatogr. A*, **795**, 43 (1998).
[18] Hong-Ping Li, Jen-Hou Li, Gwo-Chen Li, Jen-Fon Jen. *Talanta*, **63**, 547 (2004).
[19] J.W. King, Z. Zhang. *Anal. Bioanal. Chem.*, **374**, 88 (2002).
[20] S. Morais, A. Maqueira, R. Puchades. *Anal. Chem.*, **71**, 1905 (1999).
[21] L. Gamiz-Gracia, A.M. Garcia-Campana, J.J. Soto-Chinchilla, J.F. Huertas-Perez, A. Gonzalea-Casado. *Trends Anal. Chem.*, **24**, 927 (2005).
[22] J.-J. Aaron, A. Coly. *Analusis*, **28**, 699 (2000).
[23] J.F. Huertas-Perez, A.M. Garcia-Campana, L. Gamiz-Gracia, A. Gonzalez-Casado, M. del Olmo Iruela. *Anal. Chim. Acta*, **524**, 161 (2004).

[24] G.Z. Tsogas, D.L. Giokas, P.G. Nikolakopoulos, A.G. Vlessidis, N.P. Evmiridis. *Anal. Chim. Acta*, **573**, 354 (2006).
[25] T. Perez-Ruiz, C.M. Lozano, V. Tomas, J. Martin. *Anal. Chim. Acta*, **476**, 141 (2003).
[26] J.J. Soto-Chinchilla, L. Gamiz-Gracia, Ana M. Garcia-Campana, L. Cuadros-Rodriguez. *Anal. Chim. Acta*, **541**, 113 (2005).
[27] C. Ristori, C. Del Carlo, M. Martini, A. Barbaro, A. Ancarani. *Anal. Chim. Acta*, **325**, 151 (1996).
[28] K. Stein, G. Schwedt. *Anal. Chim. Acta*, **272**, 73 (1993).
[29] L. Pogacnik, M. Franko. *Talanta*, **54**, 631 (2001).
[30] P. Skladal, G.S. Nunes, H. Yamanka, M.L. Ribeiro. *Electroanalysis*, **9**, 1083 (1997).
[31] A. Nabi, M. Yaqoob, M. Anwar. *Lab. Robot. Automat.*, **11**, 91 (1999).
[32] M. Yaqoob, A. Nabi, P.J. Worsfold. *Anal. Chim. Acta*, **510**, 213 (2004).
[33] D.W. King, H.A. Lounsbury, F.J. Millero. *Environ. Sci. Technol.*, **29**, 818 (1995).
[34] A. Waseem, M. Yaqoob, A. Nabi. *Talanta*, **71**, 56 (2007).