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Analytical strategy photodegradation/chemiluminescence/continuous-flow multicommutation methodology for the determination of the herbicide Propanil

J.R. Albert-García [b], M. Catala Icardo [a], J. Martínez Calatayud [b,*]

[a] *Department of Chemistry, Polytechnic University of Valencia, Valencia, Spain*
[b] *Department of Analytical Chemistry, University of Valencia, Valencia, Spain*

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Abstract

The present paper is dealing with an analytical strategy based on coupling photodegradation, chemiluminescence and multicommutation continuous-flow methodology for the determination of the pesticide Propanil, a common herbicide. The pesticide solution is inserted as small segments sequentially alternated with segments of the solution for adjusting the suitable medium for the photodegradation. Both flow-rates (sample and medium) are adjusted to required time for photodegradation, 2.0 min; and then, the resulting solution is also sequentially inserted as segments alternated with segments of the oxidizing solutions system, 1.00×10^{-4} mol l^{-1} potassium permanganate in 2.00 mol l^{-1} sulphuric acid medium. The calibration range, from 10 μg l^{-1} to 25 mg l^{-1}, resulted in a linear behaviour over the range 10 μg l^{-1}–5 mg l^{-1} and fitting the linear equation: $I = 780.30C + 95.28$; correlation coefficient 0.9999. The limit of detection was 8 μg l^{-1} and the sample throughput 20 h^{-1}. After testing the influence of a large series of potential interferents the method is applied to water samples obtained from different places and to one formulation. The method is valid for the determination of other pesticides from the same chemical family, namely: alachlor, flumetsulam, furalaxyl and ofurace. Calibration graphs, limits of detection, repeatability and determination in water samples are obtained for each reported pesticide.

Keywords: Pesticides; Chemiluminescence; Photoreaction; Multicommutation

1. Introduction

To fight against environmental impact through the massive use, even abuse, of pesticides is proposed a strategy based on the new and emergent continuous-flow methodology known as multicommutation [1]. The manifold is provided with a luminometer; a detector allowing the analysis of low amounts of pesticide in environmental samples and wide linear calibration ranges over several orders of magnitude. The third basis of this strategy is the irradiation with UV-lamps, a simple, effective and clean analytical procedure.

From a conceptual point of view and comparing with FIA [2], the main contributions of the multicommutation to the flow-analysis is the substitution of "volumes" of insertion by "times" of insertion, which allows to develop time-based sampling methods; and, the notion of the flow assembly like a system active, versatile and easy to reshape. The fundamental device in multicommutation is the three-way solenoid valve acting as an independent commutator controlled by computer. The use of solenoid valves allows the easy, complete automation of the process (resulting in high reproducibility) with low sample and reagent consumption (economy and simplicity). Even more, the small size of solenoid valves and electronic interfaces permits the development of compact, integrated systems and of portable equipment for on-site analyses.

Analytical interest in liquid-phase chemiluminescence (CL) is continuously growing over the last 20 years; the best demonstration of this interest is the large number of recent manuscripts dealing with analytical applications for inorganic and organic (like drugs or pesticides) substances in a variety of industrial, clinical and environmental matrices. Analytical advantages of CL include high sensitivity, very low limits of detection and a wide linear range [3].

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* Corresponding author. Tel.: +34 96 354 40 62; fax: +34 96 354 40 62.
E-mail address: jose.martinez@uv.es (J.M. Calatayud).

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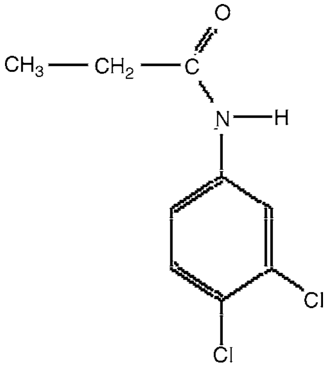

Fig. 1. Molecular structure of Propanil.

Analytical applications of liquid-phase chemiluminescence were extensively obtained involving well known CL reagents (luminol, acridinium esters, peroxyoxalates, dioxetanes, tris(2,2′-bipyridyl)ruthenium(II) etc.) in which the analyte interacts with the CL reaction, usually as a reagent, a catalyst, a quencher and even as a enhancer [4]. At present a relevant alternative to obtain and exploit determinations, which involve chemiluminescence emission from the analyte, which is the substrate in the CL. When this is not possible, a previous chemical transformation of the analyte is required; in this context, photochemical reactions (irradiation with UV–vis lamps) offer a powerful means for obtaining derivatives with improved chromophoric, fluorophoric or electrolytic properties [4–6].

Propanil or 3′4′-dichloropropionanilide (molecular weight 218.08), is a crystalline brown powder, commercially available under different branch names [7,8]. The molecular structure is depicted in Fig. 1.

Propanil is stable in aqueous solution in high concentration; however it hydrolyzes in strong acid or alkaline media. Its solubility in water is quite high, 225 mg l^{-1} at 25 °C, and it is also soluble in organic solvents like benzene, ethanol, acetone and cycle-hexane and at minor scale in toluene and xylene. Melting point of the solid is over the range 81–91 °C.

It is an herbicide of general use and moderately toxic, it is skin and eyes irritant. It is used for potatoes, rice and wheat. It could be extremely toxic for plants when mixed with carbamates or organo-phosphor pesticides. Its high aqueous solubility results in a potential high pollution in environmental water.

Most reported methods for the analytical determination of Propanil are dealing with chromatographic methods, liquid or gas, provided with different detection systems. HPLC with UV–vis absorption spectrometer was used for the determination of Propanil in a certain number of matrices; namely, sediments [9,10], plants [11], water [12–15] drinks [16] and serum [17,18]. Provided with a mass spectrometer HPLC has been applied to water [19–21] and fruits [22]. Other published procedures are dealing on Gas Chromatography for samples like water [23–27], biological fluids [28–30] and plants [31]. Other non-chromatographic analytical methodologies employed for Propanil determination include immunoassays in different modalities; a paper was dealing on aqueous solutions of Propanil for monitoring drinking water samples without requiring sample preconcentration or separation [32]; an immunoaffinity solid-phase extraction sorbent with high affinity was applied to Propanil and for structurally related phenylurea herbicides [33]; a fluorescence polarization immunoassay procedure proposed the use of a preliminary solid-phase extraction step for sample pre-concentration [34]. An amperometric sensor was fabricated for Propanil determination by coating a metallo porphyrin as a thin layer on a vitreous C electrode [35]. The electrochemical oxidation of Propanil has been also reported [36].

This paper presents a new photo-chemiluminescent system for the determination of Propanil in water samples and one formulation. The light from a low-pressure mercury lamp is used as a clean, reproducible and inexpensive "reagent" for the derivation of the pesticide, performed in acetic-acetate buffer at pH 4.8. Then, the photo-products from irradiation are oxidised by permanganate in sulphuric acid solution. On the other hand, the use of solenoid valves allows the easy, complete automation of the process with low sample and reagent consumption. To the authors knowledge, this is the first chemiluminescence-photodegradation based determination of Propanil to be reported and also the first using "multicommutation" continuous-flow methodology for its automated quantitation.

2. Experimental

2.1. Reagents and apparatus

All reagents used were analytically pure unless stated otherwise and prepared in water purified by reverse osmosis and then deionised (18 MΩ cm) with a Sybron/Barnstead Nanopure II water purification system provided with a fibber filter of 0.2 μm pore-size. The Propanil was acquired from Dr. Ehrenstorfer (99.5% purity). Other used pesticides tested as interferents, alachlor, furalaxyl, flumetsulam, metosulam y ofurace were obtained from the same manufacturer. Other reagents used were: strong inorganic acids and alkalis; oxidants as $KMnO_4$, $Ce(NH_4)_2(NO_3)_6$, H_2O_2 (all of them from Panreac, Spain); buffers, tensoactives and sensitizers: Triton X-100, *N*,*N*-dimethylformamide and $Na_2B_4O_7\cdot 10H_2O$ from Panreac; β-cyclodextrine (Fluka, Buchs, Switzerland) NH_3, Na_2HPO_4, NH_4Cl, $FeSO_4$, $FeNO_3\cdot 9H_2O$ and sodium acetate from Probus; H_2O_2, ethanol and acetonitrile from Prolabo and Merck; KH_2PO_4, NaOH, HCl and acetic acid from J.T. Baker; sodium dodecyl sulphate and hexadecylpiridinium chloride from Fluka; glycine and acetone from Guinama. Exchange resins: Duolite C20 (Probus), strong cationic, and Amberlite XAD-4 (Fluka), strong anionic.

The flow manifold, depicted in Fig. 2, consisted of a PTFE coil of 0.8 mm internal diameter; a Gilson (Worthington, OH, USA) Minipuls 2 peristaltic pump provided with pump tubing from Elkay (Co, USA); and, three solenoid valves Model 161T031 (Nresearch, Northboro, MA, USA). The photo reactor consisted of a 150 cm length and 0.8 mm internal diameter. PTFE tubing (from Omnifit) helically coiled around a 15 W low-pressure mercury lamp (Sylvania) for germicidal use. The flow-cell was a flat-spiral quartz tube of 1 mm i.d. and 3 cm total

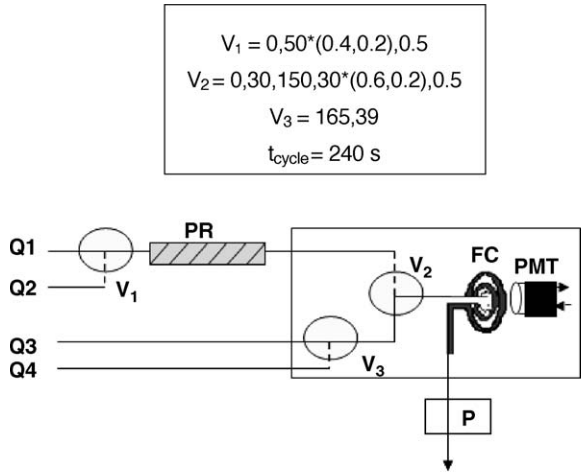

Fig. 2. Flow assembly for chemiluminescent determination of Propanil Q_1, aqueous solution of the pesticide; Q_2, buffer for the photodegradation (0.06 M acetic acid/0.14 mol l^{-1} sodium acetate at pH 4.8); Q_3, oxidative system 1×10^{-4} mol l^{-1}, $KMnO_4$ in 2.00 mol l^{-1} H_2SO_4; Q_4, water. V_1,V_2 and V_3, solenoid valves; PR, photo-reactor; PMT, photo multiplier tube; FC, flow-cell; P, peristaltic pump (flow-rate 10 ml min^{-1}); B. On top, solenoid program for preliminary assays, previous to optimization.

diameter backed by an aluminium mirror for maximum light collection. The photo-detector work-package was a P30CWAD5F-29 Type 9125 photomultiplier tube (PMT) supplied by Electron Tubes operating at 1280 V; it was located in a laboratory-made black painted light-tight box. The output was fed to a computer equipped with a counter-timer, also supplied by Electron Tubes.

3. Results and discusion

3.1. Preliminary assays

First experience was a screening to test the susceptibility of the pesticides to present chemiluminescent emission being or not irradiated with UV light. Tested pesticides were from the anilide family, namely: alachlor, flumetsulam, furalaxyl, metosulam, Propanil and ofurace. The assays were performed with lamp ON and lamp OFF and irradiation time of 2 min and 30 s on solutions containing 50 mg l^{-1} of pesticide. Different chemical media were used for the photodegradation tests: namely, H_2O, 0.05% H_2O_2, 6×10^{-5} mol l^{-1} Fe (III), 6×10^{-5} mol l^{-1} Fe (II) and 10^{-3} mol l^{-1} NaOH. After being irradiated the resulting solutions were segmented with the solution containing 7×10^{-4} mol l^{-1} potassium permanganate in 2.00 mol l^{-1} sulphuric acid medium. No light emission was observed with lamp OFF; however the chemiluminescent emission was clearly observed with lamp ON, especially high was the emission with Propanil.

A further experiment testing the chemiluminescent activity of the different pesticides was performed with pesticide concentrations over the range 1–25 mg l^{-1} versus different oxidants [6×10^{-3} mol l^{-1} Ce (IV), 7×10^{-4} mol l^{-1} MnO_4^- both of them in 2.0 mol l^{-1} H_2SO_4 and 6×10^{-3} mol l^{-1} $Fe(CN)_6^{3-}$ in 1.5 mol l^{-1} NaOH). Propanil presented the highest outputs with any tested oxidant and oxidation medium and being observed the highest outputs with potassium permanganate [over 90% higher than the obtained with ceric and hexacyane ferrate (III)]; due to that, Propanil was selected as a test-substance for further work. Selected oxidant was the potassium permanganate.

The kinetic stability of aqueous stock solutions of the test-substance was checked by preparing a 50 mg l^{-1} stock solution kept at 4 °C and recording everyday (up to 18 days) its UV–vis spectrum. No changes were observed in the recorded spectra.

3.2. Irradiation studies

The photodegradation of Propanil was studied [36]; however, and to the authors' knowledge, neither the substrate nor its reaction products have to date been determined using a chemiluminescent reaction. The reported published paper used aqueous solutions containing 10 mg l^{-1} of Propanil and TiO_2 as photocatalyst; the resulting mixture was placed into a pyrex tubing and O_2 bubbling was forced at 15 ml min^{-1}; the irradiation was restricted to 290 nm produced by a xenon lamp and selected through glass optical filters. The photo-reaction study covers the kinetics and identification of both intermediate organic products and the stoichiometry formation of inorganic products; like organic chlorine into chloride; organic sulphur to sulphate; oxidation of nitrogen to nitrate and mineralization of carbon to CO_2. A study photolysed several herbicides (monuron, diuron, linuron, metobromuron and propanil by UV-lamp or sunlight irradiation reported the production of halogenated biphenyls [37].

The photodegradation can be carried out in different chemical media and experimental conditions resulting in anilide derivatives up to the total degradation; on the other hand, the resulting photo-fragments and their concentration is critically dependent either the chemical media and the irradiation interval; due to it, we tested both parameters together. Experiments were performed with 5 mg l^{-1} of Propanil being the oxidant 7×10^{-4} mol l^{-1} MnO_4^- in 2.0 mol l^{-1} sulphuric acid. Tested media (acids, buffers and bases), time intervals and results are depicted in Table 1.

Optimum irradiation interval was for any tested medium over the range 2.0–2 min 30; periods over 3.0 min resulted in decreasing chemiluminescent outputs probably due to formation of non chemiluminometric photo-fragments. The 0.06 mol l^{-1} acetic acid–0.14 mol l^{-1} sodium acetate buffer presented the same general behaviour being all the outputs higher than any other tested approximately (over 60% of the outputs obtained with 2×10^{-3} mol l^{-1} sulphuric acid or 50% the phosphate buffer). A different behaviour was observed with the 0.5 mol l^{-1} NaOH medium in which the output was decreasing with increasing intervals probably due to basic hydrolysis of the pesticide. Selected irradiation time and medium were 2 min and acetic-acetate buffer at pH 4.8, respectively.

Influence of the temperature on the photodegradation was tested by placing the flasks containing sample, photodegradation medium and carrier into a water bath (model Tectron 200 from Selecta) and temperatures studied were room level (20 °C), 40, 60 and 80 °C. The effect of temperature was a continuous

Table 1
Tested media and time periods of photodegradation (solutions containing 5 mg l^{-1} of Propanil)

Time of irradiation (min)	H_2SO_4 0.5 mol l^{-1} (pH 0.9)	H_2SO_4 0.002 mol l^{-1} (pH 2.2)	Acetic acid 0.06 mol l^{-1}/sodium acetate 0.14 mol l^{-1} (pH 4.8)	KH_2PO_4 0.026 mol l^{-1}/ Na_2HPO_4 0.041 mol l^{-1} (pH 7.0)	Glycine buffer 0.1 mol l^{-1} (pH 8.5)	Borate buffer 0.0125 mol l^{-1} (pH 9.5)	Ammonium 0.02 mol l^{-1}/ ammonia 0.18 mol l^{-1} (pH 10.5)	NaOH 0.002 mol l^{-1} (pH 10.5)	NaOH0,5 mol l^{-1} (pH 13)
1.0	569	875	1640	1219	829	625	977	776	1052
1.5	922	1093	2050	1373	937	721	1057	819	999
2.0	1440	1377	2170	1652	1092	891	1260	888	869
2.5	1836	1418	2090	1342	1000	900	1202	839	741
3.0	1690	1295	1955	1221	980	702	793	813	688
3.5	1548	1332			970			802	
4.0	1357							711	

decrease of the output when temperature rises. Room temperature was selected for further work.

3.3. Chemiluminescent system

3.3.1. Effect of sensitizers and surfactants

The chemiluminescence emission of analytical systems can be enhanced by using a sensitizer or a micellar medium [38]. We studied the substances and concentrations depicted in Table 2. All substances used in these tests were added to the sample solution.

Only small increases were observed, excepted when 1×10^{-4} mol l^{-1} quinine was added to the sample solution in which an increase of about 900% was observed; however, the presence of quinine also resulted in low reproducibility especially for small quantities of pesticide. The new assay avoided the quinine passage through the photo-reactor by adding it either to the carrier stream or to oxidant solution; no significant increases in analytical outputs were observed in both cases.

3.3.2. Influence of oxidant concentration, oxidation medium and temperature

Fig. 3 illustrates the effect of the sulphuric acid concentration and the potassium permanganate concentration. The studied acid range, up to 3.0 M, revealed an increase of the analytical signal with increasing sulphuric acid concentration up to 2.0 mol l^{-1}, and then it makes a plateau. A concentration of 2.0 mol l^{-1} was selected in order to avoid using too concentrated solutions and hence potential deterioration of the manifold.

Usually the potassium permanganate concentration is a very critical parameter [38]; maybe due to the absorption or dispersion of the emitted light for higher oxidant concentrations. See Fig. 3 bottom; the adopted concentration for further work was 1.0×10^{-4} mol l^{-1}.

Temperature can have a relatively complex effect on chemiluminescent systems [39]; chemiluminescent reaction can be affected by temperature in both thermodynamic and kinetic terms; in this case the same considerations should be applied to the photo-reaction. On the other hand, a temperature rise can decrease the emission intensity through an increased probability of deactivation via external conversions. The influence of temperature was achieved by immersing the flasks containing the oxidant and the carrier into a water bath; the temperatures studied were room level (20 °C), 40, 60 and 80 °C. No clear increases in analytical outputs were obtained and room temperature continued to be preferred.

Flow and chemical variables affected to the outputs; these flow parameters are considered interrelated and they were optimised by a multivariate method. The modified simplex method (MSM) [40,41], was selected and the studied parameters and ranges were: total flow-rate (photo-degraded sample plus oxidant), 7.5–12.0 ml $\min^{-1}$; number of segments sample-oxidant from solenoid valve V_2, 20–40; and, time ON and time OFF (s); 0.1–0.5 and 0.4–0.8 ON and OFF, respectively. Chemical parameters were kept constant. After obtaining 15 vertices the system did not merit further investigation and the three vertices resulting in higher outputs were pre-selected for further

Table 2
Study of the influence of organized media and sensitizers (5 mg l^{-1} Propanil) at two different periods of irradiation (2 and 2.5 min)

Tensoactive	β-cyclodextrin 1.2%	*N*-cetyl-*N*,*N*,*N*-trimethyl amonium 0.2%	Benzalconium chloride 0.6%	Hexadecilpiridinium chloride 0.2%	SDS 1.2%	Triton X-100 0.6%
Irradiation time (min)						
2	3309	2015	1639	2776	996	1085
2.5	3422	1888	1909	3442	972	738

Sensitizer	*N*,*N*-dimethyl formamide 5%	Ethanol 20%	2-Propanol 20%	Acetonitrile 20%	Quinine 10^{-4} M	Formic acid 0.5%
Irradiation time (min)						
2	672	2537	3995	400	18241	657
2.5	690	1949	2967	431	10770	890

All results must be compared with the reference output (solution containing only pesticide) 1946 and 2049 for 2.0 and 2.5 min, respectively.

optimisation assays to select the one providing the best compromise sensitivity (peak height)—sample throughput (base-peak width)—reproducibility (rsd%). Selected parameters were flow-rate 10 ml min^{-1} and for the solenoid valves as follows:

$V_1 = 0.15^*(0.4, 0.2), 0.5$
$V_2 = 0, 9, 120, 30^*(0.6, 0.2), 0.5$
$V_3 = 115, 4$
$t_{\text{cycle}} = 180\,\text{s}$

3.4. Analytical figures of merit

The proposed method allows Propanil concentrations between 10 μg l^{-1} and 25 mg l^{-1} to be determined, being the linear observed range from 10 μg l^{-1} to 5 mg l^{-1}. The analytical signal and the Propanil concentration in the linear range are related by the following equation: $I = 780.30C + 95.28$ ($r^2 = 0.9999$).

The reproducibility of the slope of the calibration was determined during 7 days with freshly prepared solutions; the mean slope was 780.12 with a rsd (%) of 3.5.

The rsd for the peaks, which is a measure of repeatability and reproducibility, was determined by using reagent in 17 consecutive insertions of the same solution of 0,25 mg l^{-1} Propanil; with a calculated rsd (%) of 2.9. The experiment was repeated on 7 different days with freshly prepared solutions, the mean rsd obtained being 4.9%. The limit of detection, which was taken to be the lowest pesticide concentration that yielded a signal equal to the blank signal plus three times its standard deviation, was 8 μg l^{-1}. The sample throughput was of 20 samples h^{-1}. The sample and reagent volumes required to obtain a peak were about 0.66 and 0.33 ml, respectively.

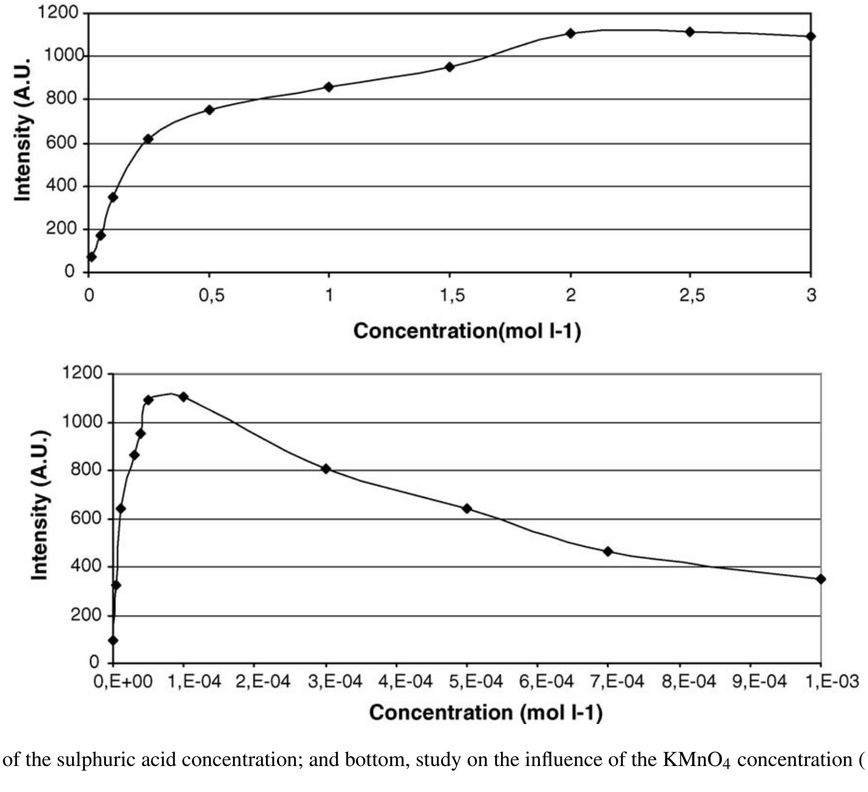

Fig. 3. Up, influence of the sulphuric acid concentration; and bottom, study on the influence of the $KMnO_4$ concentration (1 mg l^{-1} of Propanil).

Table 3
Influence of foreign compounds

Interferent	C ($\mathrm{mg\,l^{-1}}$)	R.e. (%)
Inorganic cations		
Fe^{3+}	500[a]	−3.9
Fe^{2+}	500[a]	4.5
Mn^{2+}	50	−3.2
Cu^{2+}	0.5	5
Zn^{2+}	500[a]	0.3
Pb^{2+}	500[a]	−2.4
Ni^{2+}	200	−3.5
Co^{2+}	20	−0.4
Cd^{2+}	20	−5.0
Cr^{3+}	100	−2.8
$CrO_4{}^{2-}$	1	4.4
Mg^{2+}	500[a]	−0.3
Ca^{2+}	500[a]	−1.4
K^+	500[a]	−5.0
Na^+	500[a]	−3.7
$NH_4{}^+$	500[a]	0.2
Inorganic anions		
$H_2PO_4{}^-$	0.5	−1.3
$CO_3{}^{2-}$	500[a]	−0.1
Cl^-	500[a]	−3.1
CN^-	500[a]	−3.1
I^-	5	−1.3
$SO_4{}^{2-}$	500[a]	−3.1
$NO_2{}^-$	0.2	−4.9
$NO_3{}^-$	500[a]	−3.2
CH_3COO^-	500[a]	2.7
Pesticides		
Metosulam	5	0.1
Furalaxyl	0.2	5
Flumetsulam	0.5	2.9
Ofurace	0.5	3.7
Alachlor	0.5	4.6

The solutions were prepared from salts of sodium or chloride for anions and cations, respectively.

[a] Maximum assayed concentration.

Table 3 shows the results of the study of potential interferences with the proposed method as applied to aqueous samples. Solutions of various anions, cations and pesticides containing $0.5\,\mathrm{mg\,l^{-1}}$ of Propanil were used for this purpose. The relative errors listed in the table are the differences between the signals provided by insertions of such solutions and one containing the same concentration of pesticide in pure water. When the error exceeded 5%, a lower concentration of the potential interferent was tested.

Table 4
Origins and recoveries of the spiked water samples

Type of Sample	Sample procedency	Recovery (%) ($n = 3$)
River	1°10′12.686″W; 39°31′27.99″N; Magro river (San Juan, Valencia, Spain)	99 ± 3
Residual water	0°26′19.057″W; 39°27′10.642″N; (Chirivella, Valencia, Spain)	102 ± 4
Underground water	1°9′9.993″W; 39°31′22.096″N; (San Antonio, Valencia, Spain)	97 ± 1
Mineral water	Agua de Bejis; (Bejís, Castellón, Spain)	103 ± 1

Different anions and cations studied were found to interfere with the determination. Therefore, for application to water samples, nitrites, iodide, phosphate and cupric should be removed by passage through appropriate ion-exchange resins; Amberlite XAD-4 (Fluka) (anionic) or Duolite C20 (Probus, cationic). The exchangers were prepared by packing Omnifit 5 cm × 4 mm i.d. methacrylate chromatographic columns with the resins. Prior to use, each column was conditioned by passage of a $0.1\,\mathrm{mol\,l^{-1}}$ NaOH or HCl solution. Their performance was checked with all of ions reported as interferent [$10\,\mathrm{mg\,l^{-1}}$ of ion] for this purpose; the signals provided by the reference solution [Propanil $0.5\,\mathrm{mg\,l^{-1}}$] were compared with those yielded by identical solutions additionally containing the ion concerned. All the results were quite favourable.

The applicability of the proposed method, based on a photoreaction and the chemiluminescence phenomenon, was checked by analysing samples of different types and origin. All water samples were spiked with $100\,\mathrm{\mu g\,l^{-1}}$ of Propanil within the linear range of the method. See Table 4 for results; recoveries were over the range 97.1 and 102.9% and no sample pre-treatment was required.

Commercially available formulations contain the pesticide (or pesticides) as active compound and other inert compounds as emulsifiers, dispersing or co-adjuvant agents. No commercial samples can be acquired from local manufacturers and then it was prepared in the lab with relative amounts according to legal rules (Environmental Protection Agency, EPA, code GCPF) [42]. The added amounts were: Propanil, 60%; Talc, 20%, magnesium stearate, 10%; and starch, 10%. The found amount was $0.247 \pm 0.0037\,\mathrm{mg\,l^{-1}}$ (added, $250\,\mathrm{\mu g\,l^{-1}}$); with a relative error 1.2%.

Table 5
Analytical figures of merit for other Pesticides chemically related with Propanil

Analytical results	Alachlor	Flumetsulam	Furalaxyl	Ofurace
Linear equation (correlation coefficient)	$77.48X + 62.41$ (0.9989)	$115.09X + 37.41$ (0.9995)	$88.46X + 58.48$ (0.9999)	$51.86X + 54.05$ (0.9998)
LOD ($\mathrm{\mu g\,l^{-1}}$) (criteria 3σ)	41	25	34	58
Repeativity, dsr ($n = 17$) (%)	2.9	1.9	3.5	2.3
Recovery (%) river	98 ± 2	105 ± 4	98 ± 2	98 ± 2
Recovery (%) residual water	95 ± 4	99 ± 1	102 ± 2	96 ± 3
Recovery (%) underground water	100 ± 2	101 ± 2	95 ± 4	102 ± 2
Recovery (%) mineral water	99 ± 2	97 ± 3	96 ± 3	102 ± 2

Finally, the optimised procedure was applied to other pesticides of the anilide family to obtain the usual analytical figures of merit, namely: linear equation (correlation coefficient); limit of detection, repeatability and recovery in water samples from different origins. Results are depicted in Table 5.

4. Conclusions

The analytical strategy for pesticides determination and based on the marriage photoreaction plus chemiluminescence and multicommutation flow methodology is successfully applied to determine Propanil in water samples and one formulation. Samples, in acetic-acetate buffer, are irradiated with a low-pressure mercury lamp for 150 s and the irradiation product is oxidized by permanganate in a sulphuric acid medium to obtain chemiluminescent emission that is detected by a photomultiplier tube.

Finally, the use of solenoid valves allows the easy, complete automation of the process with low sample and reagent consumption. A short discussion about the possible irradiation products is also included. The method is successfully applied to other pesticides from the same chemical family: alachlor, flumetsulam, furalaxyl and ofurace.

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