Catalá Icardo, M.; López Paz, JL.; Asensio Martín, V. (2012). Development of a Flow Injection Manifold for Napropamide Determination by Photo-Induced Chemiluminescence. Analytical Letters. 45:872-882. doi:10.1080/00032719.2012.655679.

DEVELOPMENT OF A FLOW INJECTION MANIFOLD FOR NAPROPAMIDE DETERMINATION BY PHOTO-INDUCED CHEMILUMINESCENCE

Mónica Catalá-Icardo*, José Luis López-Paz, Víctor Asensio-Martín
Instituto de investigación para la Gestión Integrada de Zonas Costeras, Escuela Politécnica Superior de Gandía, Universidad Politécnica de Valencia. C/ Paranimf nº 1, Grao de Gandía, 46730, Valencia, Spain
* Corresponding author. Email: mocaic@qim.upv.es. Tel: ++34962849333; fax: ++34962849309.

Abstract

A new, fast and simple method is proposed for the determination of the pesticide napropamide by photoinduced chemiluminescence detection coupled with a flow injection analysis (FIA) system. The emission was obtained by oxidation, with periodate in basic medium, of the photoproducts, generated on-line by UV irradiation (254 nm) of napropamide in acidic SDS (sodium dodecyl sulfate) medium. The flow method, in combination with the solid phase extraction (SPE) performed off-line with C_{18} cartridges, allowed the determination of this pesticide over the 0.8–14.0 μg L^{-1} range, with a limit of detection of 0.3 μg L^{-1}. The relative standard deviation (n=9) at 2.5 μg L^{-1} level was 4.3% for the combined FIA-SPE system. After testing the influence of several potential interfering compounds, including ions and other pesticides, the method was successfully applied to the determination of napropamide in spiked water samples with recoveries between 96-103%.

Keywords: Chemiluminescence; flow injection; napropamide; photoreaction; pesticides

INTRODUCTION

Napropamide (*N*,*N*-diethyl-2-(1-naphthalenyloxy)propanamide) is widely used for control of annual grasses and broad leaf weeds as a pre-emergent amide herbicide (Tomlin 1994). It inhibits root development and growth.

Napropamide degradation in soil by micro-organisms is slow, but its transformation into naphthoxypropionic acid is almost total (Tomlin 1994). Its photolysis rate is reduced in soil or sediments in relation to aqueous solution, due to a screen effect depending on particle size distribution. However, no dependence of this rate on organic matter content was found by Aguer et al. (2000) after light irradiation in the 300-450 nm interval. On the other hand, several researchers have concluded that the complex formation between napropamide and dissolved organic matters derived from soils have a strong effect on the sorption and desorption of napropamide from soils (Zhang 2010).

Few methods have been reported on the determination of napropamide. Most of them are chromatographic methods: high-performance liquid chromatography (HPLC) in tandem with diode array detection (Li 2006; Trajkovska 2003; Ye 2010) or mass spectrometry (MS) (Fenoll 2009; Greulich 2008), or gas chromatography (GC) (Smalling, 2008; Walorczyk 2008; Wang 2008; Cunha 2007; Passeport 2010), usually with MS.

Some authors have tried to find other alternative methods, avoiding the separation, which has led to the development of some photoluminescencent strategies. The native fluorescence of napropamide was used for G. Stangl et al. (1994) in their studies dealing with the use of cloud-point extraction with surfactants. Afterwards, Murillo-Pulgarín et al. (2003) developed a method based on fluorescence detection in sodium dodecyl sulfate (SDS) medium buffered at pH 7.2. Finally, the method proposed by Tang et al. (2004) was based on supramolecular interaction between napropamide and β-cyclodextrin, to form an inclusion complex (1:1 stoichiometry), which enhanced significantly the fluorescence intensity.

In order to increase the selectivity, Murillo-Pulgarín et al. (2002) demonstrated the viability of chemical deoxygenation micelle-stabilized room-temperature phosphorimetry for napropamide analysis in soil. SDS, thalium (I) and sulfite were used as enhancers. The organized medium protected it from the eventual presence of quenchers in the solution; the heavy atom produced an efficient spin-orbit coupling that favoured the phosphorescence; the sulfite acted as a deoxygenating agent. However, this method took at least 10 min just for stabilizing and deoxygenating the samples. Salinas Castillo et al. (2005) developed a fast heavy-atom-induced room-temperature phosphorescent system without need of organized media. These authors, used iodine as a heavy atom to obtain the phosphorescence response, which was instantaneous and remained stable for at least 1 h.

However, to the authors´ knowledge, no method based on either chemiluminiscent (CL) detection or flow injection methodology, has been previously reported for napropamide determination. Only an extended abstract with some preliminary results of the present work was recently published (Catalá-Icardo 2010).

EXPERIMENTAL

Reagents and apparatus

All reagents used were analytically pure and prepared in water deionised (18 MΩ-cm) (Millipore, Bedford, MA, USA). The napropamide was acquired from Riedel-de Haën (99.8% purity). Other pesticides used were: amitrole, metazachlor, metalaxyl, thiacloprid, DNOC and cyromazine (99.9%), 2,4-D and pirimicarb (99.6%), diquat monohydrate (99.4%), glyphosate and quinmerac (99.2%), fenamiphos (97.7%), diuron (99.5%), imazalil (99.8%) and MCPA (98.7%), all from Riedel-de Haën; methomyl (99.5%) from Chem Service; and, dimethoate (99.4%) and diphenamide (99.9%) from Fluka.

The flow manifold consisted of PTFE coil of 0.8 mm i.d. (from Omnifit); Gilson (Worthington, OH, USA) Minipuls 2 peristaltic pump provided with pump tubing from Restec; and, 6-port medium pressure injection valve (Upchurch Scientific, Model V-450). A solution of napropamide in 0.12 M SDS and 0.02 M H_2SO_4 flowed trough a photoreactor consisted of a 400 cm length of the PTFE tubing helically coiled around a 15 W low-pressure mercury lamp (Sylvania), at 2.6 mL min^{-1}. A volume of 750 μL of this solution was inserted into a water carrier stream (13.7 mL min^{-1}) which mixed with a oxidant solution of 1.7 10^{-4} M KIO_4 in 1.65 M NaOH (4.6 mL min^{-1}). The flow-cell was a flat-spiral glass tube of 1 mm i.d. and 3 cm total diameter. The photo-detector work-package was a P30CWAD5F-29 Type 9125 photomultiplier tube (Electron Tubes) operating at 1280 V, located in a laboratory-made black painted light-tight box.

Analyte solutions

100 mg L^{-1} stock solution of napropamide was prepared in 0.15 M SDS due to its small solubility in water (72 mg L^{-1}). This solution was protected against light and was stable for at least two weeks. The working standard solutions were prepared daily by diluting the stock solution and adding 0.6 M SDS and 1 M H_2SO_4 to obtain 0.12 M and 0.02 M concentrations, respectively.

Treatment of samples

Water samples from different origins (sea, spring, mineral and tap waters) were collected in plastic flaks at 4ºC, filtered over a 0.45 μm membrane filter (Sartorius, Goettongen, Germany) and analysed before 48 h. Three different concentrations (1.5, 2.5 and 4.0 μg L^{-1}) were tested in triplicate.

The cleaning and preconcentration step was performed off-line using a vacuum system and solid phase cartridges Bond Elut-C_{18}, 200 mg, from Varian. The cartridges were conditioned by passing through 3.0 mL of methanol, 3.0 mL of acetonitrile, 3.0 mL of methanol and 9.0 mL of water. The samples were passed through the cartridge at 5 mL min^{-1}. Then the cartridge was cleaned with 9.0 mL of water and dried by passing air for 20 minutes. Napropamide was eluted by gravity with 1.0 mL of acetonitrile and then under vacuum; finally 1 mL of water was passed through the cartridge to recover the remainder. Both volumes were collected in a volumetric flask of 10 mL and then SDS and H_2SO_4 were added before filling up with deionised water.

RESULTS AND DISCUSSION

Selection of the oxidative system

The natural or photoinduced chemiluminescence (PICL) emission of 20 mg L^{-1} napropamide was studied employing strong oxidants. The chemical media used for the photodegradation were: H_2O, 0.1 M H_2SO_4 and 0.1 M NaOH.

Two aditional Y-shaped pieces were added to the manifold in order to mix the oxidant (1.25 mL min^{-1}) and oxidation medium (1.25 mL min^{-1}), and the napropamide (2.1 mL min^{-1}) and photodegradation medium (0.6 mL min^{-1}) in situ. After 45 s of irradiation, the resulting solution was inserted into a carrier of water (4.9 mL min^{-1}) which merged with the oxidant systems tested: $KMnO_4$, Ce(IV), KIO_4 and $K_2S_2O_8$ in 2 M H_2SO_4, and $K_3Fe(CN)_6$, N-bromosuccinimide, H_2O_2, NaClO, KIO_4 and $K_2S_2O_8$ in 2 M NaOH. All oxidants were 8 10^{-3} M except permanganate (1.4 10^{-3} M) and N-bromosuccinimide (4 10^{-2} M).

A strong PICL signal was found with $K_3Fe(CN)_6$/NaOH, KIO_4/NaOH and H_2O_2/NaOH, being sulfuric acid the best irradiation medium. The effect of concentrations of $K_3Fe(CN)_6$ (6 10^{-3}-1.2 10^{-2} M), KIO_4 (10^{-4}-8 10^{-3} M) and H_2O_2 (6 10^{-3}-0.25 M), all of them in 2 M NaOH, was tested using 3 mg L^{-1} solution of napropamide. KIO_4 10^{-3} M provided the best results (signals 2.3 and 5.1 times higher). Moreove the effect of NaOH concentration (oxidative medium) was tested over the 0.5-4.0 M range with 1 mg L^{-1} of napropamide, being 2 M the optimum value.

The global flow rate was varied over the 7.3-22.5 mL min^{-1} range preparing periodate and NaOH together without need of confluence. The signal increased

throughout the range studied, although minimally from 20.4 mL min^{-1} onwards; consequently this value, which corresponded to 15.4 and 5.0 mL min^{-1} for carrier and oxidant respectively, was chosen.

Irradiation studies

The SDS concentration in which napropamide was prepared, might affect both, irradiation and oxidation steps. Hence, its effect was studied over the range 0.05-0.20 M, with 0.4 mg L^{-1} napropamide. But as the signal increased in the interval, so did the blank, especially from 0.15 M onwards. Subsequently, a concentration of 0.15 M SDS was selected.

Sulfuric, perchloric, hydrochloric, phosphoric, nitric and acetic acids were assayed as irradiation media at different concentrations, being 0.1 M sulfuric acid finally selected.

The residence time of the pesticides in the photo-reactor was controlled by changing flow rates of sample and irradiation medium streams. The analytical signal decreased only by 22% when the flow-rate of the pesticide was increased over the 1.55–2.9 mL min^{-1} range. Hence, a flow-rate of 2.2 mL min^{-1} was chosen (irradiation time of 55 s) since it provided a higher sample throughput.

Influence of organized media and sensitizers

A wide variety of compounds described in the literature (Catalá-Icardo 2003) as potential CL enhancers were examined. A confluence was added in the manifold, in order to mix napropamide (0.5 mg L^{-1} in 0.033 M H_2SO_4 and 0.15 M SDS at 1.65 mL min^{-1}) with the sensitizer under study (0.55 mL min^{-1}) before the lamp. It allowed to check its influence both, in the photoreaction and in the oxidation. With the aim to observe the effect only in the CL reaction, a second confluence was placed after the lamp to introduce the sensitizer (0.55 mL min^{-1}).

Several organized media were assayed instead of SDS, namely hexadecyltrimethylammonium bromide, triton X-100, hexadecylpyridinium chloride (HPC) and β-cyclodextrin. As the pesticide was not soluble in the substances tested (except in HPC), their effect was assayed by adding the sensitizer to the aliquot of napropamide 100 mg L^{-1} prepared in SDS. The only compound that provided an enhancing effect and negligible blank signals was β-cyclodextrin. However, the output achieved was significantly lower than that provided by SDS.

Other substances assayed were: ethanol 10%, acetone 1%, acetonitrile 25%; a mixture of 25% acetonitrile and 1% acetone; 1,4-dioxane 10%; formic acid 1%; 2-propanol 25%; H_2O_2 0.01, 0.02, 0.03, 0.04 and 0.06%; sodium sulfite 6 10^{-4}, 3 10^{-4} and 10^{-4} M; quinine 3 10^{-4} and 7.5 10^{-5} M; 8-hydroxyquinoline 10^{-4} M; riboflavin 10^{-5}, 5 10^{-5}, 10^{-4}, 2 10^{-4} and 4 10^{-4} M; fluorescein 10^{-4} and 10^{-5} M; and, orange acridine 10^{-4} and 2 10^{-5} M. The catalytic effect of some cations (6 10^{-5} M) was also studied, namely: Fe^{2+}, Cu^{2+} and Mn^{2+}. As increases below 20% were obtained their use was discarded.

Influence of the temperature and insertion volume and re-optimization

The effect of the temperature was studied by immersing carrier and oxidant lines and the sample loop, into a thermostated bath at 21ºC, 41, 59 and 76 ºC. As only small improvements were obtained for high temperatures, room temperature was chosen.

The signal increased with the injected volume over the range 508–759 μL, and above this value remained practically constant. A value of 759 μL was therefore chosen.

Finally, some parameters were re-optimized around the previously selected values, employing 0.15 mg L^{-1} of napropamide. Table 1 shows the optimization range and selected parameters.

Table 1. Parameters re-optimized

Parameter	Range	Selected
[KIO_4], M	$4\ 10^{-5} – 8\ 10^{-4}$	$1.7\ 10^{-4}$
[NaOH], M	1.2 – 2.0	1.65
[SDS], M	0.08 - 0.16	0.12
[H_2SO_4], M	0.015 - 0.035	0.02
Sample flow rate, mL min^{-1}	0.95 - 3.45	2.6[a]
Flow rate (CL reaction), mL min^{-1}	14.0 - 20.5	18.3[b]

[a] Corresponding to 46 s irradiation

[b] Corresponding to 13.7 and 4.6 mL min^{-1} for carrier and oxidant channels respectively

NAPROPAMIDE PHOTODEGRADATION MECHANISM

Molecular irradiation can led to the formation of fragments with smaller molecular weight (fotolysis) or to induce photocyclization, photoisomerization, photooxidation and photoreduction (Catalá-Icardo 2008).

Chang et al. (1991), working with water solutions buffered at pH 7 and employing a xenon arc lamp and sunlight, identified as major photoproducts of napropamide N,N-diethyl-1-hydroxy-α-methyl-2-naphthaleneacetamide (27%) and N,N-diethyl-4-hydroxy-α-methyl-1-naphthaleneacetamide (20%), and N,N,N′,N′-tetraethyl-4,4′-dihydroxy-α,α′-dimethyl[1,1′-binaphthalene]-3,3′-diacetamide (9%), as a minor product probably resulted from the coupling of the first primary product. Aguer et al. (1998), working with an aqueous solution irradiated at 253.7 nm, confirmed previous results for the mean photoproducts. They also detected the formation of 1-naphthol, but they do not detect the dimer, possibly because either it was formed in a second stage of the reaction or because only UV detection was employed. The increased toxicity observed after the irradiation, was probably due to the formation of naphtol. The same photoproducts found by Aguer et al. (1998) were detected by Da Silva et al. (2008) when the pesticide was irradiated with UV light or sunlight radiation on solid supports: cellulose and silica surfaces. However, when molecular oxygen was present, 1,4-naphthoquinone became a major product.

This photorearrangement has been found for several aromatic herbicides (Boule 2002) and a radical mechanism has been proposed. 1-naphthyl alkyl ethers proceed mainly from their excited singlet states via homolytic scission of the C-O bond between the naphtoxy and alkyl moieties or from induced photooxidation. The aliphatic radical released reacting on the positions of highest spin density, in the *ortho* or *para* position. This substitution is usually called photo-Fries rearrangement.

On the other hand, when surfactant photosensitization reactions are involved, significant increases in the rate of herbicidal degradation should be observed, especially with aryl-containing surfactants (Tanaka 1981). The photo-Fries rearrangement of esters and amides has been studied in micelle systems. Both, the cage and preorientational effects by SDS micelles, resulted in the regioselective formation of *o*-migration

products with higher yields than those observed in organic solvents (Kataji 2008). This can give support to the hypothesis that the major photoproducts above-mentioned could have been obtained under the conditions reported in the proposed method.

ANALYTICAL APPLICATIONS

Analytical characteristics

Under the optimum conditions, two linear intervals were found: from 20 to 350 μg L^{-1} the equation $I=(13.5\pm0.5)C-(0.28\pm0.06)$ ($r^2=0.9933\pm0.0016$, n=5); and from 0.35 to 4 mg L^{-1}, the equation $I=(16.4\pm1.1)C+(900\pm300)$ ($r^2=0.9992\pm0.0006$, n=5) were fitted, where the CL intensity (I) is expressed in Hz, and the concentration of napropamide (C) in μg L^{-1}.

The limit of detection, defined as the average blank peak height plus 3·SD, was 5 μg L^{-1} and was experimentally determined.

The RSD for 0.15 and 1.0 mg L^{-1} napropamide were 1.5 and 1.1% respectively (n=21), and the throughput 120 h^{-1}. The day-to-day reproducibility was established calculating the RSD for the slopes of five calibration curves, which were 3.7 and 6.7% for the first and second linear interval, respectively.

In order to increase the sensitivity of the method and remove ionic potential interfering species, SPE was used. Since organic solvents can affect either the CL emission or the photoreaction step, tedious procedures are usually required for their elimination. Calibration graphs (20-350 μg L^{-1} of napropamide) in 10 and 20% of methanol, ethanol and acetonitrile were performed. Bearing in mind that a 70% of decrease in the slope was observed when methanol and ethanol were employed, a 10% acetonitrile solution was considered as a good option for eluting the pesticide, as only a slight decrease of 14.8% ($I=(11.5\pm0.4)\ C - (0.057\pm0.016)$ ($r^2=0.996\pm0.002$, n=5)) in the slope was obtained in this case.

Six solutions of 100 mL of napropamide, between 2 and 20 μg L^{-1}, were treated as described in *Treatment of samples* section. The average of recoveries was (99±4)%, demonstrating the viability of the proposed strategy for the pre-concentration of napropamide.

The limit of detection was experimentally determined as 0.3 μg L^{-1} after treatment of 250 mL of sample; the dynamic range was 0.8–14 μg L^{-1} and the RSD for a 2.5 μg L^{-1} solution of napropamide was 4.3% (n=9).

Study of interferences

The interfering effect of foreign species commonly present in natural waters was investigated adding the potential interferents to 0.2 mg L^{-1} of napropamide. The results obtained for the highest concentrations assayed are summarised in Tables 2 and 3.

Good tolerance was generally observed, but some ions yielded an important interference, namely Ca^{2+}, Mg^{2+}, NO_2^- and NO_3^-, being the maximum concentrations tolerated (error in brackets): 8 (-4.5%), 8 (-5.0%), 0.08 (+3.6%) and 0.5 mg L^{-1} (+4.2%), respectively.

Table 2. Study of interfering ionic species

Interferent	Concentration (mg L^{-1})	Error (%)
Na^+	9829	-1.2
Cl^-	15171	-1.2
K^+	1000	-1.8
Ca^{2+}	1000[a]	-5.3
Mg^{2+}	200[a]	-5.3
NH_4^+	100	-0,3
SO_4^{2-}	1000	+1.8
CH_3COO^-	100	+0.6
$H_2PO_4^-$	100	+4.3
HCO_3^-	500	-1,5
NO_2^-	10[a]	5.4
NO_3^-	200[a]	5.4
Urea	100	+1.9

[a] Sample was passed through a C_{18} cartridge

The SPE strategy proposed was successfully applied for the removal of those ions treating 250 mL of 8 μg L^{-1} napropamide together with them at the concentrations indicated in Table 2 as described in *Treatment of samples* section.

Table 3. Interfering effect of pesticides

Common name	Chemical group	[pesticide]/[napropamide][b]	Error (%)
Amitrole	Triazole	10	-1.6
Carbaryl	Carbamate	2	+4.7
Cyromazine	Triazine	10	+2.8
2,4-D	Alkylchlorophenoxy	10	-3.5
Dimethoate	Organophosphate	10	+3.7
Diphenamid	Alkanamide	6	+4.0
Diquat monohydrate	Bipyridylium	10[a]	+1.7[a]
Diuron	Phenylurea	1	-4.7
Fenamiphos	Organophosphate	2	+3.9
Glyphosate	Phosphonoglycine	10	+2.1
Imazalil	Imidazole	10	+3.1
MCPA	Aryloxyalkanoic acid	10	+0.3
Metalaxyl	Phenylamide	10	+0.7
Metazachlor	Chloroacetamide	10	+1.4
Methomyl	Carbamate	10	-4.8
Pirimicarb	Carbamate	10	-2.5
Quinmerac	Quinoline	10	+4.3
Thiacloprid	Neonicotinoid	2	+4.7

[a] Sample was passed through a C_{18} cartridge

[b] 8 μg L^{-1} or 0.2 mg L^{-1} of napropamide was used with and without SPE, respectively

A great selectivity was found when 18 pesticides, from different chemical groups (http://agrochemicals.iupac.org), were tested (Table 3), since only diquat showed a big interference, despite CL from the oxidation products of some of the assayed pesticides had been previously reported (Meseguer-Lloret 2010; Catalá-Icardo 2011; López-Paz 2009; He 2006; Murillo Pulgarín 2006). Hence, it was necessary to decrease diquat concentration until to a 1:4 diquat:napropamide ratio to obtain an error of +4.6%. However, due its ionic character, it was possible to remove diquat efficiently using SPE with C_{18}.

The good selectivity and sensitivity of the developed method make it suitable for the determination of napropamide in most of natural waters. However, more complex matrixes, with high concentrations of organic matter, as residual waters or soils, could require a previous separation with C_{18} cartridges, since that matter, if eluted, could consume the oxidant used as a reactive.

Applications

250 mL of water were spiked with different concentrations of napropamide (1.5, 2.5 and 4 μg L^{-1}) in triplicate. The recoveries achieved using the proposed SPE-FIA method were: (103±10)% for spring water; (103±6)% for tap water; (96±4)% for sea water; and (99±5) and (101±7)% for two different mineral waters.

CONCLUSIONS

A new FIA-PICL procedure for the determination of the herbicide napropamide is presented. It was based on the irradiation of napropamide in an acidic SDS medium with UV light and the subsequent oxidation of its photoproducts with periodate in basic medium. The FIA method presented a competitive throughput (120 h^{-1}) and a detection limit of 5 μg L^{-1}, together with a good selectivity. The system was implemented with a C_{18} SPE cartridge, which apart from the removal of interferent ions, allowed to achieve a detection limit of 0.3 μg L^{-1}, value close to the European Union (EU) maximum permitted levels, established in 0.1 and 0.5 μg L^{-1} for individual compounds and total pesticides, respectively (European directive 80/778/EEC 1993).

The analytical characteristics of other luminescent methods reported for napropamide determination were compared in Table 4. The basis of those methods is discussed in the *Introduction* section. As can be seen, the limit of detection obtained in the proposed method is competitive with those previously reported, even without sample pretreatment. To the authors´ knowledge, it is the first time that the chemiluminometric properties of photoproducts from napropamide have been reported.

Table 4. Comparison between luminescent methods for napropamide determination

Analytical Method	Lineal range ($\mu g\ L^{-1}$)	Detection limit ($\mu g\ L^{-1}$)	Pre-concentration method	Reference
Fluorimetry	10-100 100-2000	4.2	Liq-liq	(Passeport 2010)
Fluorimetry	3.7-1500	1.1	Liq-liq	(Stangl 1994)
Fluorimetry	-	0.101	CPE	(Cunha 2007)
MS-RTP	50-600	16.0	Liq-liq	(Murillo Pulgarin 2003)
HAI-RTP	3.2-600	3.2	No	(Tang 2004)
PICL	20-350 350-4000	5	No	This work
PICL	0.8-14	0.3	SPE	This work

MS-RTP: micelle-stabilized room-temperature phosphorescence
HAI-RTP: heavy-atom-induced room-temperature phosphorescence
PICL: photoinduced chemiluminescence
Liq-liq: liquid-liquid extraction
SPE: solid phase extraction
CPE: cloud point extraction

Acknowledgment
This work was supported by the Ministry of Education and Science of Spain (Project CTM2006-11991) and FEDER funds.

REFERENCES

Aguer, J.P., P. Boule, F. Bonnemoy, and J.M. Chezal. 1998. Phototransformation of napropamide [*N,N*-diethyl-2-(1-naphthyloxy)pro-pionamide] in aqueous solution: influence on the toxicity of solutions. *Pestic. Sci.* 54:253-257.

Aguer, J.P., L. Cox, C. Richard, M.C. Hermosin, and J. Cornejo. 2000. Sorption and photolysis studies in soil and sediment of the herbicide napropamide. *J. Environ. Sci. Health B* 35:725-738.

Boule, P., L. Meunier, F. Bonnemoy, A. Boulkamh, A. Zertal, and B. Lavedrine. 2002. Direct phototransformation of aromatic pesticides in aqueous solution. *Int. J. Photoenergy* 4:69-78.

Catalá-Icardo, M., M. Misiewicz, A. Ciucu, J.V. García-Mateo, and J. Martínez-Calatayud. 2003. Flow injection-online photochemical reaction for direct chemiluminescence determination of photodegraded chloramphenicol. *Talanta* 60:405-414.

Catalá-Icardo, M. and J. Martínez-Calatayud. 2008. Photo-induced luminescence. *Crit. Rev. Anal. Chem.* 38:118-130.

Catalá-Icardo, M., J.L. López-Paz and V. Asensio-Martín. 2010. FI-Photoinduced chemiluminescent determination of napropamide herbicide. *Luminescence* 25:235.

Catalá-Icardo, M., J.L. López-Paz and A. Peña-Bádena. 2011. FI-Photoinduced chemiluminescence method for diuron determination in water samples. *Anal. Sci.* 27:291-296.

Chang, L.L., B.Y. Giang, K. Lee, and C.K. Tseng. 1991. Aqueous photolysis of napropamide. *J. Agric. Food Chem*. 39:617-621.

Cunha, S.C., S.J. Lehotay, K. Mastovska, J.O. Fernandes, M. Beatriz, and P.P. Oliveira. 2007. Evaluation of the QuEChERS sample preparation approach for the analysis of pesticide residues in olives. *J. Sep. Sci.* 30(4):620-632.

Da Silva, J.P., E.V. Bastos, L.F.V. Ferreira, and R.G. Weiss. 2008. Surface photochemistry of the herbicide napropamide. The role of the media and environmental factors in directing the fates of intermediates. *Photochem. Photobiol. Sci.* **7**:69-75.

European directive 80/778/EEC. 1993. Brussels. European Commission.

Fenoll, J., P. Hellin, C.M. Martinez, and P. Flores. 2009. Multiresidue analysis of pesticides in soil by high-performance liquid chromatography with tandem mass spectrometry. *J. AOAC Int.* 92(5):1566-1575.

Greulich, K. and L. Alder. 2008. Fast multiresidue screening of 300 pesticides in water for human consumption by LC-MS/MS. *Anal. Bioanal. Chem.* 391(1):183-197.

He, S.H., D.Y. He and Z.J. Zhang. 2006. Determination of pirimicarb by flow injection combined with chemiluminescence. *Fenxi Huaxue* 34(11):1622-1624.

International Union of Pure and Applied Chemistry. Global availability of information on agrochemicals. http://agrochemicals.iupac.org (accessed in June 2011).

Katagi, T. 2008. Surfactant Effects on Environmental Behavior of Pesticides. *Rev. Env. Contam. Toxicol.* 194:71-177.

Li, J.Z., X.G. Chu, H.X. Cai, J. An, and Q. Yang. 2006. Simultaneous determination of residues of 12 amide herbicides in soybeans by high performance liquid chromatography. *Sepu* 24(6):585-588.

López-Paz, J.L., M. Catalá-Icardo and B. Antón-Garrido. 2009. Determination of diquat by flow injection–chemiluminescence. *Anal. Bioanal. Chem.* 394:1073-1079.

Messeguer-Lloret, S., S. Torres-Cartas and M.C. Gómez-Benito. 2010. Flow injection photoinduced chemiluminescence determination of imazalil in water samples. *Anal. Bioanal. Chem.* 398:3175-3182.

Murillo-Pulgarin, J.A. and L.F. García-Bermejo. 2003. Determination of napropamide in technical formulations, soil and vegetable samples by sensitized fluorescence: validation of the method. *Anal. Chim. Acta* 491(1):37-45.

Murillo-Pulgarín, J.A., A. Alanon-Molina, and P. Fernández-López, P. 2006. Automatic chemiluminescence-based determination of carbaryl in various types of matrices. *Talanta* 68(3):586-593.

Passeport, E., A. Guenne, T. Culhaoglu, S. Moreau, J. Bouyé, and J. Tournebize. 2010. Design of experiments and detailed uncertainty analysis to develop and validate a solid-phase microextraction/gas chromatography–mass spectrometry method for the simultaneous analysis of 16 pesticides in water. *J. Chromatogr. A* 1217(33):5317-5327.

Salinas-Castillo, A., J.F. Fernández-Sánchez, A. Segura-Carretero, and A. Fernández-Gutiérrez. 2005. Simple determination of the herbicide napropamide in water and soil samples by room temperature phosphorescence. *Pest. Manag. Sci.* 61:816-820.

Smalling, K.L. and K.M. Kuivila. 2008. Multi-residue method for the analysis of 85 current-use and legacy pesticides in bed and suspended sediments. *J. Chromatogr. A* 1210(1):8-18.

Stangl, G. and R. Niessner. 1994. Cloud point extraction of napropamide and thiabendazole from water and soil. *Mikrochim. Acta* 113:1-8.

Tanaka, F.S., R.G. Wien, and E.R. Mansager. 1981. Survey for Surfactant Effects on the Photodegradation of Herbicides in Aqueous Media. *J. Agric. Food Chem.* 29:227-230.

Tang, B., W.L. Liu, Y. Wang and Z.Z. Chen. 2004. Studies on the supramolecular interaction between napropamide and β-cyclodextrin by spectrofluorimetry and its analytical application. *Anal. Chim. Acta* 509(2):145-150

Tomlin C. (ed.), 1994. The Pesticide manual. Bath, UK: 10th edn. British Crop Protection Council, The Bath Press.

Trajkovska, V., S. Petrovska-Jovanovi, and M. Cvetkovski. 2003. Solid-phase extraction and HPLC/DAD for the determination of some pesticides in wine. *Anal. Lett.* 36(10):2291-2302.

Walorczyk, S. 2008. Development of a multi-residue method for the determination of pesticides in cereals and dry animal feed using gas chromatography-tandem quadrupole mass spectrometry: II. Improvement and extension to new analytes. *J Chromatogr A* 1208(1-2):202-214.

Wang, L.B., C. Li, C.F. Peng, X.Q. Li, and C.L. Xu. 2008. A rapid multi-residue determination method for herbicides in grain by GC-MS-SIM. *J. Chromatogr. Sci.* 46(5):424-429.

Ye, Y.Q., N. Wu, H.T. Huang, G.Y. Yang, and Q.F. Hu. 2010. Determination of Some Pesticides in Tobacco Leaf by High Performance Liquid Chromatography and Sample Preparation with Matrix Solid Phase Dispersion. *Asian J. Chem.* 22(5):3659-3663.

Zhang, R., J. Cui, H.M. Zhu, and H. Yang. 2010. Effect of Dissolved Organic Matters on Napropamide Availability and Ecotoxicity in Rapeseed (Brassica napus). *J. Agric. Food Chem.* 58:3232-3240.