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Photo-induced Fluorescence of Fluometuron in a Continuous-flow Multicommutation Assembly

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Abstract This paper deals with the photo-induced fluorimetric determination of the herbicide Fluometuron with the aid of a continuous-flow assembly of the emergent and new methodology known as Multicommutation which was provided with an on-line photoreactor. Maximum fluorescence intensity was observed at basic pH solutions, 1×10^{-4} mol l^{-1} NaOH, after 1.4 min of irradiation and being the maximum at λ_{exc} 247.0 nm and λ_{em} 325.0 nm.

The influence of different experimental parameters either chemical (pH, surfactants presence, solvent polarity and temperature) or hydrodynamic (time of photo-degradation, size and number of different segments and flow-rate) was tested.

The linear dynamic range was from 0.01 to 4.0 mg l^{-1} of Fluometuron; the inter-day reproducibility (as R.S.D.) of the slope was 0.001% and 1.7% from the peaks intra-day reproducibility. A large series of potential interferents was studied and finally the method was applied to human urine, soil, formulation and water samples.

Keywords Fluometuron · Urea derived pesticides · Fluorescence · Continuous-flow · Multicommutation

Introduction

The use or even abuse of pesticides in the fight against animal and plant pests has resulted in massive pollution. In fact, most pesticides are water-soluble and can readily spread in the environment. For this reason, many countries have passed stringent legislation intended to protect citizens' health and the environment. This has raised the need to develop new analytical methods for the expeditious, inexpensive and as automatic as possible control of these compounds.

The Fluometuron [1] or 1,1-dimethyl-3-(α,α,α-trifluoro-*m*-tolyl)urea, ($C_{10}H_{11}F_3N_2O$) with a molecular weight 232.29 belongs to the phenyl urea herbicides family. It is a white to tan powder or crystalline material with an amine-like odour and it is also available in liquid, dry flowable and wettable powder formulations. Its water solubility is 105 mg l^{-1} at 20°C, and it is slightly soluble in other solvents like in acetone, chloroform, methanol, hexane, and organic solvents. Melting point is 163–164°C. The molecular structure as depicted in Fig. 1a.

Fluometuron is a selective herbicide which acts by inhibiting photosynthesis [2]; it is registered exclusively for use on cotton and sugarcane. It can be applied pre-emergence, for weed control before planting, or post-emergence, after target crops and weeds come up, and may have residual activity for several months.

Fluometuron is a mild skin irritant affecting to the mucous membrane lining the skin, gastrointestinal tract, and respiratory system; it may cause corneal opacity in test animals. This herbicide is considered a mild inhibitor of cholinesterase. Other symptoms of Fluometuron poisoning include muscular weakness, tearing or watery eyes, extreme exhaustion, and collapse. Some secondary teratogenic effects were seen in the progeny of rats and rabbits. Mice showed evidence of liver tumours and leukaemia, a condition characterized by uncontrolled growth in the number of white-blood cells. Studies on the carcinogenic effects in humans are not conclusive. Fluometuron is slowly absorbed into the body from the gastrointestinal tract. At 72 hr after rats were given oral doses of 50 mg/kg Fluometuron, 15% of the dose was excreted in the urine and 49% was excreted unchanged in the faeces. And about other ecological effects, it is slightly toxic to fish and is relatively non-toxic to bees.

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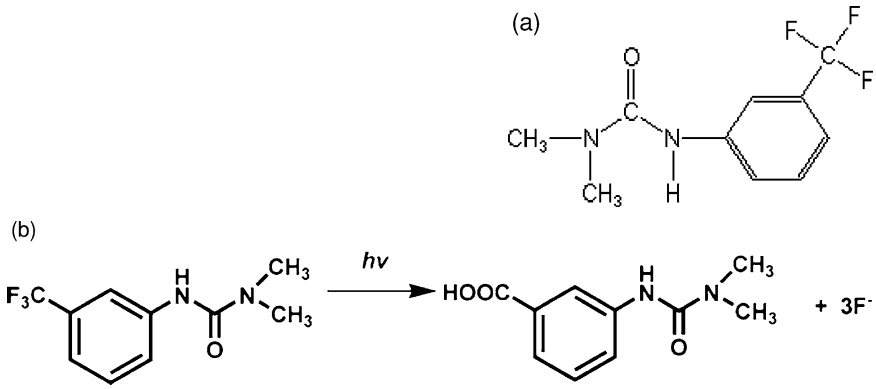

Fig. 1 (a) Molecular structure of Fluometuron. (b) Direct photolysis degradation (defluorination) of Fluometuron

Fluometuron is moderately to highly persistent in the soil environment, with a reported field half-life of 12 to 171 days. A representative field half-life under most conditions is estimated to be 85 days. Breakdown in the soil environment occurs mainly through photodegradation specially when there is little rainfall after application, and by microbial action. As it is soluble in water, it is poorly bound to most soils and may be highly persistent in the water environment. The half-life of Fluometuron in water is 110 to 144 weeks. It is stable at pH values ranging from 1 to 13, at 20°C. However, exposure of 10 mg l^{-1} aqueous solutions of Fluometuron to natural sunlight resulted in 88% decomposition in 3 days, with a half-life of 1.2 days.

Most of reported analytical procedures are dealing with separation and determination of pesticides by liquid chromatography. Complex mixtures of pesticides, even from different families, have been assayed. The chromatographic procedure should be applied after a previous solid-phase extraction step. Main efforts are devoted to test the influence of different sorbent phases and eluting reagents. Different detectors have been used [3] and mostly of reported papers are dealing on water samples.

The simultaneous determination of mixtures of herbicides has been solved by using HPLC [4]; and the separation of 10 sulfonyl- and phenylurea herbicides from one of their most common degradation products (3-chloro-4-methylphenyl urea) was also developed with the aid of liquid chromatography provided with a diode array UV detection and positive ion electrospray mass spectrometry; the best optimization of chromatographic phases resulted with a copolymer of poly(divinylbenzene-co-N-vinylpyrrolidone) [5]. A solid-phase adsorbent, based on cytokinin-binding protein immobilized on Sephadex LH-20, was synthesized and evaluated either for a solid-phase-extraction and for the HPLC column [6]. A water sample containing known amounts of sixteen phenylurea herbicides was aspirated through preconditioned C18 cartridges and separated by HPLC by using gradient elution with the solvent mixture acetonitrile and H_2O [7]. Another method for the separation of a mixture of polar pesticides in water and wine samples was developed by coupling automated in-tube solid-phase microextraction to HPLC-electrospray ionization mass spectrometry equipment [8]. In an HPLC method developed for phenylurea pesticides in surface waters, emphasis was put on the pesticide preservation by the addition of 2.5 g Trizma preset pH 7 crystals [a mixture of tris(hydroxymethyl)aminomethane and its hydrochloride] and 0.25 mg copper sulphate [9]. A Liquid Chromatography – Mass Spectrometry method was developed targeting 52 pesticides (thiocarbamates and phenylureas) without previous extraction-separation from the matrix; the chromatography system comprised a reversed-phase C8 column and an ammonium acetate water/acetonitrile binary gradient; then, the method was applied to drinking and wastewater samples [10]. A microbore liquid chromatography and positive-ion electrospray MS set was applied to the determination of pesticides and herbicides in water; the paper included a discussion on the mobile-phase matrix effects [11]. The mixture Dinoserb, Fluometuron and other terbutylazine pesticides was assayed with the aid of HPLC and by using a column with a gradient mobile phase of ammonium acetate and methanol [12]. The separation of Fluometuron and its main environmental metabolites were separated in a soil sample matrix after extraction with methanol [13]. The simultaneous determination of Fluometuron and norflurazon in soil extracts and leachates was performed on the basis of sample being extracted with methanol; after centrifugation and filtration, the soil extracts were diluted with $CaCl_2$ to give a 1:1 methanol/$CaCl_2$ matrix [14].

Several phenylurea herbicides: namely, chlorbromuron, Fluometuron, diuron, linuron, metobromuron, monolinuron and monuron were isolated from weed plant materials by extraction with acidic aqueous solutions and the corresponding aqueous extract was pre-concentrated and cleaned-up by using a continuous solid-phase extraction module; further work was the determination of the pesticides with the suitable gas chromatographic equipment provided with a mass spectrometry detector [15]. The degradation products of chlorsulfuron, chlortoluron, diuron, fluometuron, isoproturon, linuron, metabenzthiazuron, metobromuron and monuron formed in the injector of a GC instrument were

used to identify the respective herbicides; the influence of the solvent on the degradation was also studied [16–18]. A comparative study on several chromatographic procedures (gas and liquid) can be find in the analytical literature [19]. A different previous solid-phase separator was based on immunosorbents; it was applied to a mixture of phenylurea pesticides in drinking and surface water samples [20]. The immunosorbent was prepared by immobilizing anti-isoproturon antibodies and it was packed into stainless-steel columns.

Some intents dealing on thin layer chromatography (TLC) have been also reported [21]; the phenylurea herbicides chlortoluron, diuron, Fluometuron, isoproturon, linuron, methabenzthiazuron and neburon were separated with the aid of three different TLC systems; the experimental results were evaluated and densitometrically quantified at nanogram levels. Capillary electrochromatography techniques have been also proposed for separation and determination of mixtures of different herbicides (carbamates and phenylureas among others) [22, 23]; the separation was based on the potential of porous graphitic carbon as a new stationary phase.

The Capillary Electrophoresis at a potential of 25 kV and spectrophotometric detection at 190–320 nm was applied [24]; previously the sample solution was homogenized in methanol, filtered, diluted with H_2O, then subjected to solid-phase extraction (C8) and eluted with CH_2Cl_2. The separation was achieved in 7 min

A supercritical CO_2 fluid extraction of Fluometuron from soil samples was compared with the conventional liquid-liquid extraction with methanol [25]. The soil sample was treated with ^{14}C-ring-labelled Fluometuron (I) and the optimization of the supercritical extraction method also included adding modifiers and varying CO_2 fluid density.

The present work was focused to find new photo-induced fluorescence automated processes to increase the sensitivity and obtaining minor limits of detection for pesticides. The method is performed with the aid of the emergent continuous-flow analytical methodology known as Multicommutation and based on an automated solenoid-valves set. The result is a quick procedure performed in very simple assembly which also could be adapted to work in a post-column format.

To the author's knowledge, this is the first report dealing with the fluorescent-based determination of Fluometuron and also the first using a continuous-flow methodology for its automated determination.

Experimental

Reagents

All chemicals were of analytical reagent grade and solved in purified water by reverse osmosis and deionised (18MΩcm) with the aid of Sybron/Barnstead Nanopure II. Fluometuron was from Dr. Ehrenstorfer GmbH (98.5%, Germany). Other reagents were glycine for buffer solutions, ethanol, iso-propanol, acetonitrile and dimethylformamide all from Scharlau (Spain); NaCl, sodium tetraborate, NH_4Cl, sodium dodecyl sulphate and Triton X-100 all from Panreac (Spain); ammonia and HCl from Probus (Spain); N-cethyl NNN trimethyl ammonium from Merck; hexadecylpiridinium 98% and β-cyclodextrine from Fluka (Switzerland); and, benzalkonium chloride from Guinama (Spain).

Inorganic salts tested as potential interferents were NaCl, KCl, $Na_2SO_4.10H_2O$, KCN, $NaNO_3$, $FeSO_4.2H_2O$,$MgCl_2.6H_2O$ (Panreac), $Na_2H_2PO_4$ (UCB), Na_2CO_3 (Prolabo), KI (Guinama), $ZnCl_2$ (Scharlau), $Pb(CH_3COO)_2.3H_2O$, $MnCl_2.4H_2O$ (DHémio), $Co(CH_3COO)_2.4H_2O$ (Riedel de Haëdel, Germany), $Cr(CH_3COO)_3.nH_2O$ and $CuSO_4.5H_2O$ (Scharlau), $CaCl_2.2H_2O$, $NaNO_2$, $FeCl_3$, $NaCH_3COO.3H_2O$, and $NiCl_2$ all from Probus.

The flow manifold comprised PTFE tubing of 0.8 mm internal diameter, a Gilson (Worthington, OH, USA) peristaltic pump, model Minipuls 2 which was provided with flexible pump tubing from Elkay (Co, USA); and, two solenoid valves Model 161T031 (Nresearch, Northboro, MA, USA). The valves were controlled via friendly software made in the laboratory and were working in a computer type Pentium in Microsoft Windows 98. The photo reactor consisted of a 150 cm length and 0.8 mm internal diameter PTFE tubing (from Omnifit, USA) helically coiled around a 15 W low-pressure mercury lamp (Zalux) for germicidal use; and, the detector was a Fluorimeter Jasco FP-6200 provided with a flow-cell Hellma 176.052-QS (inner volume 125 μl). Data collection was performed by means of the corresponding software prepared for the fluorimeter "Spectra Manager for Windows 95/NT," type 1.53.00. The flow-manifold is depicted in Fig. 2.

As external standard used to test the fluorimeter reproducibility was a solution containing 25 $\mu g \cdot l^{-1}$ quinine in 0.1M H_2SO_4. The test was performed before and after the studies with the Fluometuron.

Results and discussion

Flow preliminary assays (screening)

We performed some preliminary tests involving various pesticides in order to study their molecular changes upon UV irradiation. To this end, we used aqueous solutions at a variable pH over the range 0–12 to record UV- vis absorption spectra before and after irradiation for 2.5 or 5 min. Tests were conducted under continuous-flow conditions, using the multicommutated system of Figure 2 and the following parameter values: flow-rate 7 ml min^{-1}; number of segments

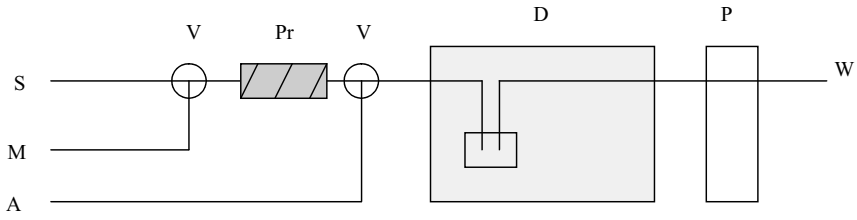

Fig. 2 Flow assembly for the fluorimetric determination of Fluometuron S, aqueous solution of analyte; M, medium; A, water; P, peristaltic pump; Pr, photo-reactor, V, solenoid valves; W, waste; D, fluorimeter FP-750 (λ_{exc} 247.0 nm and λ_{em} 325.0 nm)

10; sample and medium segment size 0.4 and 0.2 s, respectively; and irradiation time 2.5 min. Fluometuron was found to both fluoresce upon irradiation and exhibit native fluorescence (lamp OFF), with $\lambda_{exc} = 247$ nm and $\lambda_{em} = 325$ nm in both cases.

Based on the results, Fluometuron was chosen for subsequent tests as it exhibited the largest increase in emission upon irradiation. The kinetic stability of a 2 mg l^{-1} solution of the pesticide was studied by keeping it refrigerated at 4°C in the dark for 7 days. The UV-vis spectra for the solution recorded over such a period exhibited no significant changes.

Influence of pH

Both the nature of the medium and its pH can influence the fluorescence emission of a compound. We thus studied the potential effects of both variables carefully by using the above-described flow assembly.

Solutions containing a 2 mg l^{-1} concentration of the herbicide were adjusted to pH 1–12 potentiometrically by adding HCl or NaOH dropwise as required. All solutions exhibited some fluorescence, whether or not they were irradiated, but particularly those irradiated at pH 10.0.

Because the pH was strongly influential, we tested various buffer solutions in order to obtain as chemically robust as possible an irradiation medium. The buffers tested included glycine/NaOH, sodium tetraborate/NaOH and NH_4Cl/NaOH. The RSD values of the resulting peaks were 1.3, 1.1 and 0.9 for the ammonia, glycine and tetraborate buffer, respectively. As can be seen in Fig. 3, the highest signal was obtained with the alkaline solution (*i.e.* in the absence of buffer).

The influence of the NaOH concentration in the buffer was examined over the range 10^{-5}–10^{-3} mol l^{-1}, with the lamp both ON and OFF. The best results were provided by an NaOH concentration of 10^{-4} mol l^{-1}.

Influence of the photodegradation time

The extent of photodegradation of a substance (*i.e.* the cleavage of bonds in it by effect of irradiation) depends on the irradiation time. We examined the influence of this variable over the range 0.5–4 min. As can be seen from Fig. 4, the optimum irradiation time was 1.5 min, which was thus chosen for subsequent tests.

Study of the medium: solvent polarity and organized media (presence of tensoactive agents)

Fluorescence emissions can be affected by the polarity and viscosity of the medium, and also by the presence of organized media or heavy atoms, among others.

Organized media (particularly surfactants) can enhance fluorescence emission by protecting excited molecules from interactions with their environment. This protective effect is exerted by micelles wrapping up the molecules of the excited species; alternatively, such species can be protected by "storage" within appropriate molecular structures such as that of β-cyclodextrin. Tests were conducted on solutions containing a 1 mg l^{-1} concentration of pesticide plus the protective agent at a level above its critical micelle concentration (cmc) and the blank needed to record the control signal. The compounds studied and the amounts used (in a final solution volume of 50 ml) were as follows: 0.1 g of 98% hexadecyl pyridinium, 0.3 g of benzalkonium, 0.1 g of *N*-cetyl-*N*,*N*,*N*-trimethylammonium, 0.6 g of Tween 80, 0.6 g of sodium dodecyl sulphate (SDS), 0.3 g of Triton X-100 and 0.6 g of β-cyclodextrin. The results were compared with those provided by an identical Fluometuron solution containing no protective agent. The enhancing effect on the fluorescence emission was especially marked with β-cyclodextrin and SDS. However, the relative standard deviations (RSDs) were quite high as the likely result of the strong signals given by

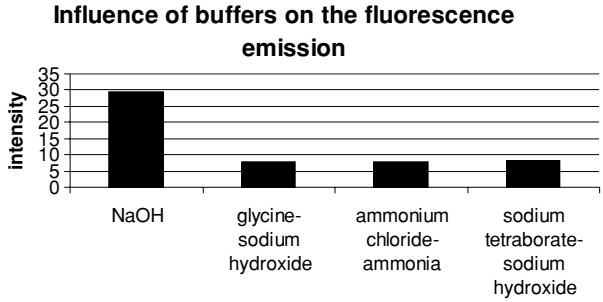

Fig. 3 Influence of NaOH and different buffers on the emission outputs. (2 mg l^{-1} of Fluometuron)

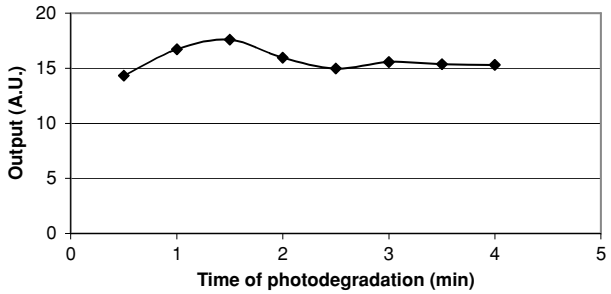

Fig. 4 Influence of photodegradation time on the fluorescent emission

the blanks. No protective agent was therefore chosen for use in subsequent tests.

We also examined the effect of organic solvents of variable polarity, which were used to prepare solutions containing a 0.5 mg l^{-1} concentration of pesticide. As can be seen from Fig. 5a, the highest, most reproducible signals were obtained in the presence of acetonitrile. A further test at variable concentrations of this solvent from 5–40% revealed a proportion of 20% to provide the best results (see Fig. 5b).

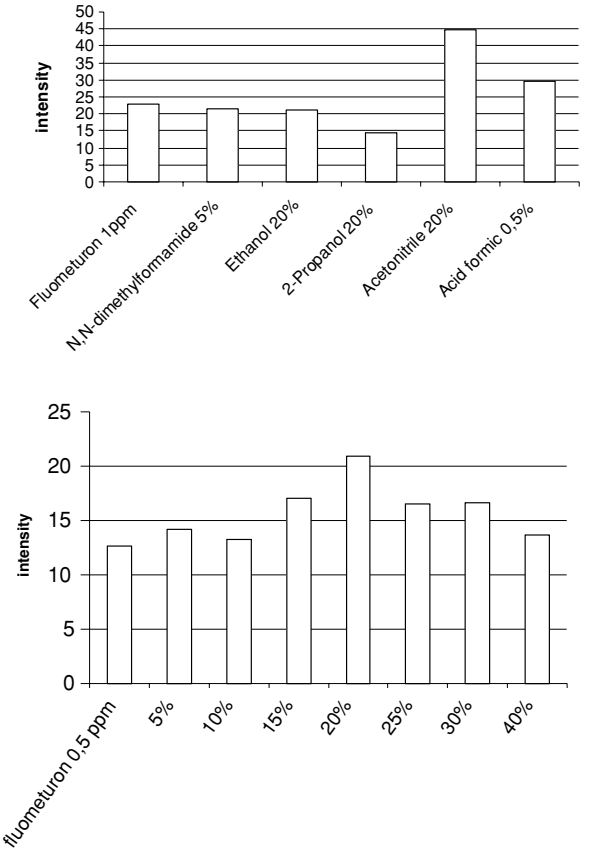

Fig. 5 Influence of the solvent polarity. (a) Studied organic solvents. (b) Influence of the acetonitrile concentration

Influence of the temperature

Raising the temperature of a fluorescence-based analytical system usually decreases the amount of light emitted through an increased likelihood of collisions between molecules or ions leading to deactivation via non-radiative mechanisms. In the presence of some derivatization reaction, the influence of temperature is much more difficult to predict as it can reach both the fluorescence emission and the derivatization process.

The effect of temperature was examined by immersing the vessels containing the sample, medium and carrier in a Tectron 200 water bath at a variable temperature from room level to 80°C. Tests showed the emission intensity to decrease strongly with increasing temperature. We therefore adopted room temperature for subsequent tests.

Photochemical reactions

The photodegradation of various substances all bearing a trifluoromethyl group on an aromatic ring was examined in recent previous work [29] where the kinetics of both direct photodegradation (*i.e.* when a compound absorbs light, becomes unstable and subsequently decomposes in the absence of other chemical means) and indirect photodegradation (when indirect photolysis occurs through interactions with reactive intermediates produced by another light-absorbing molecule).

The defluorination of the trifluoromethyl group is believed to constitute a common pathway for direct photolysis in trifluoromethylated compounds. The presence of hydroxyl groups has been shown to accelerate the kinetics of direct photolysis. Thus, photodegradation at pH 9 was found to be more than twice stronger than at any other pH tested (*viz.* 4.0, 5.5 and 7.0). The most interesting conclusion drawn as regards the direct and indirect kinetics was that the $–CF_3$ group undergoes photo-nucleophilic substitution by a carboxyl group (–COOH). A stoichiometric study of the reaction (see Fig. 1b in the previous paper [29]) revealed the presence of three fluoride ions per photolysed molecule. The reaction products were isolated and identified by LC/MS/MS. The mechanism was confirmed for other, similar compounds and further information on the influence of the -OH group in the indirect photolysis pathway was provided.

The above-described preliminary tests conducted in this work revealed that a 1 mg l^{-1} solution of the pesticide exhibited fluorescence in various photodegradation media containing Fe(II), Fe(III), hydrogen peroxide or 10^{-4} mol l^{-1} NaOH. Spectra were identical in all media, with two emission bands of different strength; the emission intensity, however, differed markedly among media. As noted earlier, the greatest intensity by far was that obtained in the NaOH medium. This is quite consistent with the results described in the

previous paragraph. Thus, the emission band at 247 and 249 nm appeared in the spectra obtained in the presence and absence of irradiation (*i.e.* with the lamp ON and OFF, respectively) and peaked at similar wavelengths (325 and 332 nm, respectively). The differences observed with the lamp OFF and ON were about 11% in favour of the latter. This justified using irradiation on the pesticide, especially if one considers the simplicity of the flow manifold including an on-line integrated photoreactor.

We thus recorded the UV-vis absorption and fluorescence spectra for Fluometuron in an alkaline solution in the absence and presence of irradiation for variable lengths of time (0.5, 1.5 and 2.5 min). The absorption spectra obtained in the alkaline medium without irradiation exhibited three bands typical of aromatic rings [30], two peaking at 207 and 241 nm, respectively, and the third appearing as a plateau over the wavelength range 268–280 nm. This last band increased with increasing irradiation time up to 1.5 min; by contrast, the other two decreased only slightly, with no clear-cut effect of the irradiation time. This suggests the substitution of a -CF_3 group on the ring by an electronegative group (–COOH).

Analytical figures of merit

The persistence of analytical outputs when the experimental conditions are altered, also known as "robustness" in relation to an analytical procedure, was examined over a range about $\pm 10\%$ around the selected optimum concentrations for sodium hydroxide and acetonitrile. Relative errors were calculated by comparing the outputs with those obtained under the reference conditions. The ranges studied were 17–23% *vs* 20% for acetonitrile and 5×10^{-5} –5×10^{-4} mol l^{-1} *vs* 1×10^{-4} mol l^{-1} for sodium hydroxide. Both concentrations proved critical (especially that of NaOH, with relative errors exceeding 10%). By exception, an increase of more than 20% in the acetonitrile concentration resulted in a relative error of 3.9%. The final set of selected flow parameters is depicted in Table 1.

The dynamic range studied spanned concentrations from 0.01 to 18 mg l^{-1} and was fitted to the equation $I = -0.9895x^2 + 48.3480x + 0.1535$ with a correlation coefficient of 0.9975. The parabolic profile obtained was linear from 0.01 to 5.0 mg l^{-1} and fitted the equation $I = 47.286x + 0.242$ with a correlation coefficient of 0.9992 for $n = 5$ (*i.e.* with 5 replicates per dot).

The reproducibility of the slope of the calibration curve or relative standard deviation was examined over the range 0.01–5 mg l^{-1} in tests performed on different days and on freshly prepared solutions. The mean slope obtained from 6 independent calibrations of Fluometuron was 41.7287 (the calculated RSD was 0.001%). The RSD for the peaks, which is a measure of repeatability, was determined by using 20 consecutive sample aliquots containing a 0.5 mg l^{-1} pesticide concentration and found to be 1.7%.

Table 1 Set of flow parameters selected for further work

$V_1 = 0,10^*(0.3,0.4)$
$V_2 = 0,7,84$
$t_{cycle} = 91s$

The maximum throughput was calculated from the average peak base width for 20 replicates containing a 0.5 mg l^{-1} concentration of analyte. The result was 33 samples/h. The limit of detection, which was taken to be the lowest pesticide concentration giving a signal equal to the blank signal plus three times its standard deviation, was 0.1 mg l^{-1}.

The analytical features of the proposed method and its tolerance to potential interferences accompanying Fluometuron in real samples were studied by using variable concentrations of interferents up to 500 mg l^{-1} and a 0.5 mg l^{-1} pesticide concentration. When the error exceeded 5%, a lower concentration of interferent was used. Foreign species were considered not to interfere when the calculated relative error with respect to the blank (*viz.* a solution containing 0.5 mg l^{-1} pesticide alone) was less than $\pm 5\%$. The results are shown in Table 2. As can be seen, the most critical adverse influence was exerted by iron (II and III), copper (II), manganese (II), chromium (III), nitrite, phosphate and sulphate ions. Therefore, these cations and anions should be removed by passage through appropriate ion-exchange resins such as Duolite A-107 (anionic) or C20 (cationic), both from Probus, if their interference with the determination of the pesticide is to be avoided.

In this work, 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 passing a 0.1 mol l^{-1} NaOH or HCl solution. Interferents were removed by preparing solutions containing a 0.5 mg l^{-1} concentration of pesticide and 300 mg l^{-1} interferent. All results were quite acceptable (see Table 2).

Nitrite ion, which interfered above 100 mg l^{-1}, can be easily removed. Thus, a solution containing 0.5 mg l^{-1} Fluometuron and 500 mg l^{-1} nitrite exhibited no interference following gentle heating for 10 min (see Table 2).

The applicability of the proposed FIA fluorimetric method was checked on various types of sample including human urine from different individuals, water from different sources, soil and a pesticide formulation.

Urine samples were directly spiked with the required amount of herbicide to obtain a Fluometuron concentration of 1 mg l^{-1} and subjected to the continuous-flow analytical procedure. The results thus obtained departed markedly from the amount of pesticide added, even when the standard

Table 2 Influence of foreign compounds (*up*); and Influence of foreign compounds after treatment of the solution (*bottom*)

Interferents	C(mg l^{-1})	Relative error (%)
Up		
Fe^{3+}	50	−5
Fe^{2+}	100	0.64
NH_4^+	500	−5.4
Mn^{2+}	500	7.6
K^+	200	4.2
Na^+	100	4.7
Zn^{2+}	500	−0.65
Mg^{2+}	500	4.3
Ni^{2+}	200	2.9
Cr^{3+}	200	6.4
Cu^{2+}	200	−6.1
Ca^{2+}	500	5.9
$H_2PO_4^-$	500	−4.1
CH_3COO^-	200	−3.2
Cl^-	200	2.9
SO_4^{2-}	500	−0.77
NO_2^-	100	4.7
NO_3^-	200	−3.1
Bottom		
Fe^{3+},Cu^{2+},Ca^{2+},Mn^{2+},Cr^{3+}	300	7.1
SO_4^{2-},$H_2PO_4^-$	300	2.7
NO_2^-(boil)	500	2.1

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

procedure was applied, probably because the sample matrix acted as an internal filter—the absorption peak of the sample matrix at 325 nm coincided with the Fluometuron emission peak. A separation step was therefore seemingly required. Various solid-liquid extraction cartridges were used for this purpose, and the absorption spectra for the solutions before passage and after elution compared. The best results (*i.e.* complete retention of the herbicide) were obtained with Bond Elut C18 cartridges from Varian and acetonitrile as eluent. These cartridges also retained part of the sample, resulting in smaller relative errors. Two consecutive retention-elution cycles sufficed to ensure good results. Recoveries ($n = 5$) were 99.0, 101.8 and 96.4%.

The applicability of the proposed Multicommutation fluorimetric method was also checked on water samples of variable origin that were all spiked with a 1 mg l^{-1} concentration of Fluometuron. The types of samples studied, their sampling location, and the recoveries obtained (plus their standard deviations) were as follows: underground water from San Antonio, Valencia, Spain (1°9′9.993″W, 39°31′22.096″N), 102.0% (1%); waste water from Xirivella, Valencia (0°26′19.057″W, 39°27′10.642″N), 103.9% (2%); tap water from the University of Valencia, 103.0% (3%); and mineral water bottled by Agua de Bejis in Castellón, Spain, 104.3% (0.5%).

Commercially available formulations of pesticides contain the active ingredient(s) plus other, inert compounds such as emulsifying, dispersing and coadjuvant agents. No commercial samples of Fluometuron were available from local pesticide manufacturers, so a wettable powdered sample had to be prepared in the laboratory from relative amounts in accordance to legal rules (Environmental Protection Agency, EPA, code GCPF) [31]. Thus, the samples contained 50% Fluometuron, 20% talc and 30% magnesium stearate. The amount of pesticide found was 1.2 mg l^{-1} (RSD 0.02%), so the recovery was 104.2%.

A soil sample was collected from an agricultural field and treated with the pesticide following the recommended procedure for pesticide application [34]. Then, a liquid extraction was performed with 100 ml of water and 20 g of soil with shaking for 20 min, after which the suspension was filtered and the filtrate monitored spectroscopically. A blank test was simultaneously conducted on an unspiked soil sample the extract from which was found to exhibit no fluorescence. The amount of pesticide recovered departed markedly from that added to the soil. Solid-liquid extraction of the extract using the same procedure as for the urine samples provided a recovery of 97.5% (RSD 4.5%), however.

Conclusions

A new analytical method based on the light-induced fluorescence of the herbicide Fluometuron and the use of the continuous-flow methodology known as "Multicommutation" is proposed. The optimum assembly includes a photoreactor and the photofragments obtained are driven to the flow-cell of a spectrofluorimeter in order to monitor emitted light.

The method requires the use of no chemical reagents for the emission to develop. Rather, the native fluorescence of the pesticide is boosted by prior irradiation. All at room temperature and pH 10.0.

The method was used for the determination of Fluometuron in various types of sample including water, soil, human urine and a pesticide formulation.

The assembly used affords the implementation of a separation technique such as liquid chromatography or electrophoresis in the post-column mode in order to further enhance the selectivity. This is a result of the ability of multicommutated systems being capable of addressing different analytical problems without the need for physical changes in the hardware, but only reconfiguration of the software.

The proposed method exhibits competitive sensitivity, with a detection limit of 0.1 mg l^{-1}, in addition to an RSD of 1.7% and a throughput of 33 samples/h.

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