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# Rapid determination of glufosinate in environmental water samples using 9-fluorenylmethoxycarbonyl precolumn derivatization, large-volume injection and coupled-column liquid chromatography

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**Abstract**

The application of 9-fluorenylmethoxycarbonyl (FMOC) derivatization prior to coupled-column LC with fluorescence detection using a reversed-phase $C_{18}$ column (C-1) coupled to an ion-exchange column (C-2) proved to be useful for the rapid determination of the very polar pesticide glufosinate in a variety of environmental water samples at the sub-ppb level. The separation power of the first column is used to provide (i) sensitivity by means of large-volume injection and (ii) selectivity by an efficient preseparation of the very polar analyte from the less polar interferences including the excess of unreacted FMOC reagent. Conditions for the important parameters with respect to separation and sensitivity, viz., sample injection volume, separation power of the columns and composition of the buffer and modifier in the mobile phases, were established, resulting in a method with which glufosinate in water samples, after FMOC derivatization, can be assayed at a level of 0.25 $\mu$g/l (signal-to-noise ratio = 3) in less than 15 min. The overall procedure has a sample throughput of more than 50 per day. Drinking, ground and surface water samples spiked at levels between 0.5 and 5.0 $\mu$g/l yielded average recoveries between 90 and 105% ($n = 5$ for each sample type and spiked level) with relative standard deviations between 1 and 5%. The method is linear over at least three orders of magnitude ($r > 0.999$). The limit of detection can be lowered to 0.1 $\mu$g/l by means of a simple preconcentration step with a Rotavapor.

## 1. Introduction

A recent report on Water Pollution published by the Commission of the European Communities [1] clearly emphasizes that information on the occurrence of a number of very polar pesticides is not yet available. The major reason for this is the lack of adequate analytical methodology to determine efficiently such very polar compounds at the sub-$\mu$g/l level in aqueous samples.

One of these "problem" analytes is glufosinate, which is used as a non-selective contact

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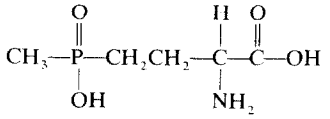
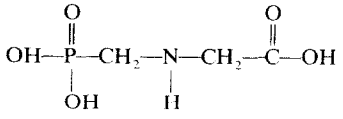
Table 1
Structural formulae and water solubilities of glufosinate and glyphosate

| Pesticide | Formula | Solubility in water (mg/l at 20°C) |
|---|---|---|
| Glufosinate |  | $2 \cdot 10^5$ |
| Glyphosate |  | $0.1 \cdot 10^5$ |

herbicide with increasing popularity in both Netherlands and Spain. As indicated in Table 1, glufosinate is a very polar compound and its structural formula is similar to that of the older and widely used herbicide glyphosate (first marketed in 1974), for which a variety of analytical residue methods are available [2–18]. Probably for reasons of later marketing (since the early 1980s) and its (so far) less widespread application, information on analytical methodology for glufosinate is poor in comparison with glyphosate. For example, official handbooks on pesticide residue analysis in foodstuffs [19,20] refer only to the analytical method supplied by the manufacturer [21]. A modification of this method [22] has been included in German official handbooks [23,24] to determine glufosinate in drinking water. However, this method is very laborious, involving enrichment on an anion-exchange column, a derivatization step and clean-up on silica gel prior to analysis by GC with nitrogen–phosphorus detection.

The aim of this study was to develop a method for the determination of glufosinate in water samples which is faster and, hence, more suitable for monitoring purposes. Regarding their chemical similarity, the published method for glyphosate was used as the starting point in method development. Glyphosate and its major metabolite aminomethylphosphonic acid (AMPA) can be determined by both GC [3–7] and LC [8–17]. Both techniques require derivatization of the analytes, necessary for the chromatographic separation in GC and improve detectability in LC with fluorescence detection. The possibility of performing derivatisation in aqueous solutions, which are compatible with both water samples and reversed-phase chromatographic separation, usually makes LC the preferred technique.

Recent work [25–27] has demonstrated that the combination of direct large-volume injection and coupled-column RPLC is a suitable technique for the rapid, sensitive and selective determination of polar pesticides in environmental water samples. As has been experimentally determined [25–27] and explained rationally [26], the applied separation power and dimensions of the first $C_{18}$ column made it possible to inject large sample volumes (sensitivity) and perform an efficient clean-up (selectivity) between the polar analyte and the large excess of UV-absorbing early interferences.

This paper reports the development of a coupled-column method for the rapid determination of glufosinate, after 9-fluorenylmethoxycarbonyl (FMOC) derivatisation, in environmental water samples using a $C_{18}$ column for efficient separation between the analyte and FMOC (and interferences) coupled to an amino column for the anion-exchange separation of the fluorescent glufosinate derivative.

## 2. Experimental

### 2.1. Chemicals

Glufosinate (content >99%) was obtained from Riedel-de Haën (Seelze, Germany). Acetonitrile and ethyl acetate, both of HPLC-grade, were purchased from Scharlau Science (Barcelona, Spain). Analytical-reagent grade potassium dihydrogenphosphate, disodium tetraborate decahydrate, orthophosphoric acid (50% pure), hydrochloric acid (37%), potassium hydroxide and 9-fluorenylmethyl chloroformate (FMOC-Cl) were bought from Merck. HPLC-grade water was obtained by purifying demineralized water in a Nanopure II system (Barnstead, Newton, MA, USA).

A stock standard solution (ca. 500 $\mu$g/ml) of glufosinate and dilutions were prepared with HPLC-grade water. A 0.025 *M* borate buffer solution (pH 9) and a 100 $\mu$g/ml FMOC-Cl solution were prepared in HPLC-grade water and acetonitrile, respectively.

Acetonitrile–0.05 *M* phosphate (pH 5.5) in water (35:65, v/v) and acetonitrile–0.1 *M* phosphate (pH 5.5) in water (35:65, v/v) were used as the first (M-1) and second (M-2) mobile phases, respectively. The pH of the aqueous buffer solutions was adjusted with 2 *M* KOH and 1 *M* HCl.

### 2.2. Equipment

The HPLC set-up is illustrated schematically in Fig. 1. The modular system consisted of a Model 1050 sampler (Hewlett-Packard, Waldbronn, Germany), the manual injector of which, equipped with a 2.0-ml loop, was used to perform large-volume injections (LVI), a Model 1050 gradient pump (P-1, Hewlett-Packard), a Model C6W six-port switching valve (HV) driven by a WE-II actuator from Valco (VIGI, Schenkon, Switzerland) and time controlled by the sampler, a Model 2150 pump (P-2) from LKB (Bromma, Sweden), a Model 1046A fluorescence detector (Hewlett-Packard) set at 263 nm (excitation) and 317 nm (emission), a 30 × 4.6 mm I.D. separation column (C-1) packed with 5-$\mu$m Nucleosil $C_{18}$ from Scharlau Science and a 250 × 4.6 mm I.D. separation column (C-2) packed with 5-$\mu$m Adsorbosphere $NH_2$ from Alltech (Carnforth, UK). C-2 was kept at 30°C in the column heater of the Model 1050 pump (P-1).

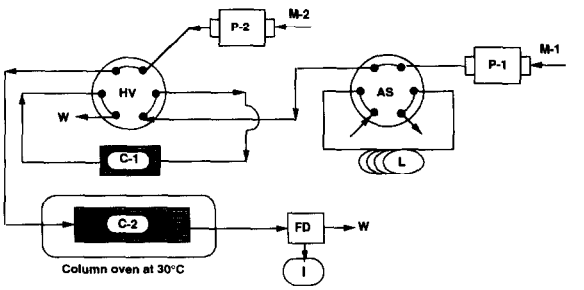



Fig. 1. HPLC set-up for column-switching. AS = sample injector with a 2-ml loop (L); HV = six-port high-pressure value; P-1 = gradient LC pump; P-2 = isocratic LC pump; C-1 = first separation column; C-2 = second separation column; M-1 and M-2 = mobile phases on C-1 and C-2, respectively; FD = fluorescence detector; I = integrator system; W = waste.

Recording of chromatograms and quantitative measurements of peak heights were performed with a Hewlett Packard HPLC Chem Station (software version G1034A). A Digilab 517 pH meter and Pipetmans (200 and 1000 $\mu$l) were obtained from Crison Instruments (Barcelona, Spain) and Gilson, respectively.

### 2.3. Sample preconcentration

To lower the limit of detection for glufosinate from 0.25 to 0.1 $\mu$g/l, 25 ml of water sample were transferred into a 250-ml round-bottomed flask and evaporated to dryness with a Rotavapor using a water-bath temperature of 40°C. The residue was dissolved in 5 ml of HPLC-grade water.

### 2.4. Precolumn derivatisation

A 0.5-ml volume of water sample or a water sample concentrated fivefold by means of

Rotavapor evaporation was pipetted into a 9-ml glass tube together with 1.0 ml of borate buffer and 1.0 ml of FMOC reagent. The tube was swirled and left at room temperature for 30 min. After reaction, 5 ml of borate buffer were added and the tube was swirled again for thorough mixing.

### 2.5. LC analysis

The mobile phases (see Fig. 1) were set at a flow-rate of 1 ml/min. A volume of 2.00 ml of the solution obtained after derivatization was injected on to C-1. After clean-up with 2.25 ml of M-1 (injection volume included), C-1 was switched on-line with C-2 for 18 s to transfer the fraction (300 $\mu$l) containing the glufosinate derivative to C-2. Two minutes after injection, C-1 was rinsed and conditioned by applying gradient elution from 35 to 65% acetonitrile in 2 min, holding at 65% acetonitrile for 2 min, then to 35% acetonitrile in 2 min. Quantification of glufosinate was done by external calibration with standard solutions of glufosinate in water which were processed with the precolumn derivatization procedure.

## 3. Results and discussion

This study was focused on the development of an efficient method for the determination of glufosinate in water samples using published information on the LC determination of glyphosate. Two different derivatization procedures for glyphosate are commonly used: (i) precolumn derivatization using FMOC reagent [8–12] and (ii) postcolumn derivatization using *o*-phthaldehyde (OPA) reagent [8,13–18]. FMOC forms easily and quantitatively derivatives with both primary and secondary amines in aqueous solutions. However, the excess of the less polar highly fluorescent reagent must be removed with an additional liquid–liquid extraction step [9–12] or with gradient elution after the RPLC separation of the analytes [8]. The recommended method for the determination of glyphosate in foodstuffs [2,15] and used in the USA as an Environmental Protection Agency method for the determination of glyphosate in drinking water [18] is based on the use of postcolumn derivatization with OPA. The non-fluorescence of unreacted OPA allows on-line derivatization of primary amines with the chromatographic separation without removing the excess of reagent. Therefore, glyphosate (secondary amine) requires postcolumn hydrolysis prior to the OPA reaction, which involves more instrumentation and careful maintenance. Moreover, the underivatized analytes are separated on an anion-exchange column, usually with a low separation power.

In contrast to OPA, FMOC reacts with both primary and secondary amines and it use does not require a previous hydrolysis step. Hence FMOC seems to be attractive for improving both the simplicity of the chromatographic set-up and the detectability. As has been shown for FMOC-glyphosate [8], the approach of precolumn derivatization with FMOC offers the possibility of separating the analyte and FMOC on a $C_{18}$ column. The applicability of column switching using a first $C_{18}$ column to perform an automated and effective clean-up prior to a selected off-line standard FMOC derivatization procedure for glyphosate [11] was investigated. The several steps in the method development are discussed below.

### 3.1. Sample pretreatment

The selected procedure [11] uses, for the complete precolumn derivatization of glyphosate and AMPA, 1 ml of aqueous sample, 1 ml of FMOC solution (1000 $\mu$g/ml in acetonitrile) and 1 ml of borate buffer and a reaction time of 20 min at room temperature. Because glufosinate is a primary amine, it can be expected that in comparison with glyphosate (secondary amine) lower FMOC concentrations can be used. Employing the same procedure, experiments showed that with a tenfold decrease in the FMOC concentration the signal of FMOC-glufosinate remained constant. Expecting some increase in selectivity towards secondary amines present in water samples and less interference of

the unreacted excess of reagent, the lower FMOC concentration was selected for further work (for the final procedure, see Experimental).

### 3.2. Separation on second column

Glufosinate forms with FMOC a derivative by reaction of the amine (analyte) and the acid chloride (FMOC-Cl), yielding an anionic compound. According to the literature [9–12], the separation of FMOC-glyphosate is preferably performed on an amino-bonded silica column in combination with aqueous phosphate solution. The important factors for the separation, viz., percentage of modifier and the ionic strength and pH of the buffer, have been discussed in detail [11]. Using this information, a 250 × 4.6 mm I.D. amino column with a mobile phase of acetonitrile–0.05 *M* phosphate in water (35:65, v/v) were selected as the initial LC conditions. Investigating the influence of the pH (tested pH range = 3–7), it appeared that the retention was maximum at pH 4 ($k' = 12$) and decreased at lower pH ($k' = 4$ at pH 3) or higher pH ($k' = 2$ at pH 7). Further, a decrease in the ionic strength (tested phosphate concentration = 0.05–0.005 *M*, pH = 5.5) increased the retention considerably ($k' = 3.3$ and 20 at 0.05 and 0.005 *M* phosphate, respectively). In this case, however, the high retention leads to excessive band broadening. Hence a decrease in ionic strength is not advantageous for improving retention. Acetonitrile–0.05 *M* phosphate (pH 5.5) in water (35:65, v/v) was therefore selected as a good compromise between separation ($k' = 4$) and the peak shape of FMOC-glufosinate. It is well known that a phosphate solution at the selected pH of 5.5 will not have any buffer capacity and therefore fluctuations in retention can be expected. At such a pH, a citrate buffer is more suitable. In comparison with phosphate, the application of a 0.05 *M* citrate (pH 5.5) solution resulted in considerable band broadening of the analyte at a similar retention. A mixture of phosphate–citrate buffer did not improve this situation. Apparently, only the presence of phosphate ions favourably influences the elution profile of FMOC-glufosinate on the amino-bonded column. Therefore, a new experiment was performed, increasing the ionic concentration to 0.1 *M* phosphate, which reduced the peak volume of FMOC-glufosinate (the retention was not affected) and provided a 25% increase in peak height. Owing to possible damage of the pistons and seals, higher salt concentrations were not investigated and 0.1 *M* phosphate was finally selected for mobile phase M-2. Increasing the column temperature (range 30–50°C) did not improve the elution profile of the analyte.

### 3.3. Clean-up procedure on first column

The first step in obtaining an efficient preseparation between FMOC and FMOC-glufosinate was to employ a small column (4 × 4 mm I.D.) packed with 5-$\mu$m $C_{18}$ (Waters–Millipore). In order to minimize disturbances of the ion-exchange separation on the second column (C-2), a mobile phase of acetonitrile–0.05 *M* phosphate (pH 5.5) in water (35:65, v/v) was selected on C-1. As discussed in earlier work [24–26], the attainable sensitivity and selectivity and selectivity of a column-switching procedure will depend on how much sample can be injected on to the first column and transferred to the second column without excessive band broadening of the analyte. Actually, two processes are crucial: (i) elution of the analyte during injection, which in this instance will be determined by the degree of retention of the analyte on $C_{18}$, and (ii) peak compression prior to transfer, which will depend on the eluotropic strength of the mobile phase(s). Applying large-volume injections, elution on C-1 must be considered as a step gradient in which the same volume acts as the first mobile phase. Consequently, the eluotropic strength (percentage of acetonitrile) of the sample solution will be a determining parameter and it should be kept as low as possible to minimize band broadening of the analyte during injection. Experiments clearly indicated that a quantitative FMOC reaction of glufosinate requires the presence of at least 40% (v/v) of acetonitrile, which is in agreement with the selected procedure [11]. Under the selected LC conditions, the maximum

sample injection volume avoiding excessive band broadening of the analyte (sensitivity) and also providing the minimum required separation between the compound and unreacted FMOC (selectivity) was about 20 $\mu$l. The sample loadability could be significantly increased by an aqueous dilution the sample prior to injection. For example, a tenfold diluted solution (with borate buffer) containing 4% of acetonitrile allowed an injection volume of 500 $\mu$l. Establishing the obtainable sensitivity and selectivity with respect to sample dilution and injection volume, a threefold dilution with borate buffer appeared to optimum (15% of acetonitrile). From this solution about 200 $\mu$l could be injected on to the $C_{18}$ precolumn, giving a marginal separation between the analyte and FMOC. Dilution with pure water or aqueous 0.05 *M* phosphate solutions (pH range 1–5) resulted in an insufficient separation between FMOC and the analyte.

In order to increase the sample loadability (sensitivity), a 5-$\mu$m $C_{18}$ column (30 × 4.6 mm I.D.) with a greater separation power than the 5-$\mu$m $C_{18}$ column (4 × 4 mm I.D.) was selected as C-1. Maintaining the same mobile phase, it appeared that large-volume injections (up to at least 1.0 ml) on this column resulted in a very favourable elution of the FMOC-glufosinate peak. It appeared that the sample mobile phase (15% of acetonitrile) results in a sufficient retention and acceptable peak volume of the analyte, whereas with the mobile phase of the column (35% of acetonitrile) the analyte elutes as an unretained compound well separated from the later eluting FMOC. This favourable elution behaviour is illustrated in Fig. 2A, showing the chromatogram obtained on C-1 of a 1-ml injection of spiked glufosinate solution (100 $\mu$g/l) diluted threefold with borate buffer after derivatization (for procedure, see Experimental).

Fig. 2B shows the chromatogram obtained for a 330-$\mu$l injection of an undiluted solution (40% of acetonitrile) containing the same amount of sample as the diluted solution (15% of acetonitrile) in Fig. 2A. The chromatograms clearly demonstrate the usefulness of the dilution step to prevent excessive peak tailing and, consequently, to improve sensitivity. Moreover, the dilution

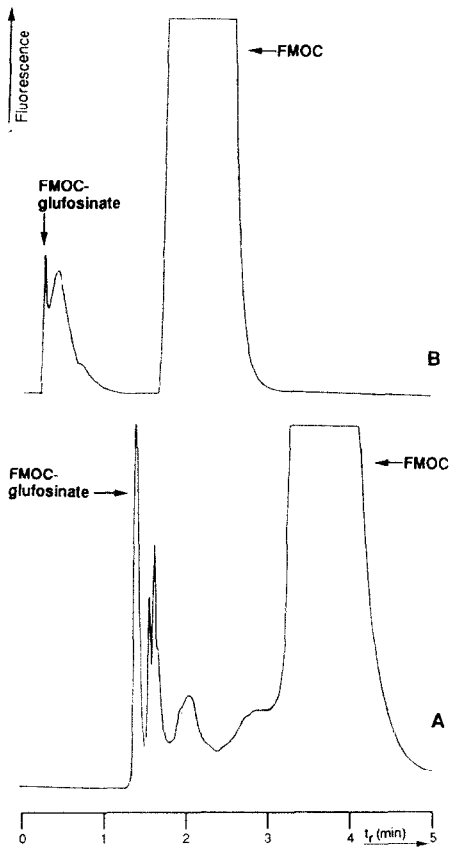



Fig. 2. Chromatograms recorded on C-1 connected to the fluorescence detector of a glufosinate standard solution (100 $\mu$g/l) obtained after FMOC derivatization. (A) 1000 $\mu$l of the solution after a threefold dilution with borate buffer; (B) 330 $\mu$l of the undiluted solution. See text for further explanation.

step allows the application of a small transfer volume (300 $\mu$l), which is favourable for the selectivity.

In order to enhance the sensitivity further, the injection of larger sample volumes (up to 4 ml) was investigated. It appeared that volumes larger than 2 ml did not substantially increase the signal of the analyte.

Fig. 3 shows the chromatogram of a 10 ppb glufosinate standard solution obtained with the proposed procedure, which employs a "clean-up" volume of 2.3 ml after injection (injection volume included) and a transfer volume of 300 $\mu$l.

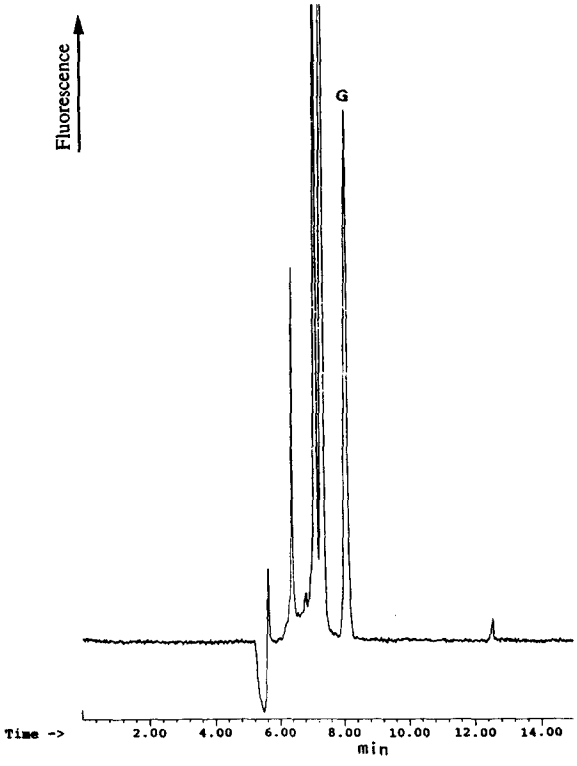



Fig. 3. Column-switching LC with fluorescence detection (FD) with large-volume (2.0 ml) sample injection of a surface water sample spiked with glufosinate at a level of 10 μg/l. For LC conditions, see Experimental.

Complete automation of the whole procedure including precolumn derivatization by means of the autosampler used seems an interesting feature. However, the maximum available volume of the autosampler vials (<1.8 ml) limited the possibility of making proper dilutions after reaction and to perform large-volume injections (2 ml). Making no concession to sensitivity, the simple off-line precolumn derivatization procedure was preferred to a completely automated procedure.

## 4. Results

The response of FMOC-glufosinate was linear for standard solutions of glufosinate in water with concentrations between 0.25 and 100 μg/l ($r = 0.9996$, $n = 5$). The described procedure (see Experimental) was validated by analysing various types of water samples spiked with glufosinate. The recoveries at several levels are given in Table 2. The performance of the procedure is illustrated in Fig. 4, which shows the LC analysis of surface water spiked with glufosinate at 1 μg/l. It appeared that for all types of water samples the resulting chromatograms were very similar, rendering a sensitive and selective procedure. Partly owing to good reproducibility of the chromatographic patterns, the limit of detection was found to be 0.25 μg/l (signal-to-noise ratio = 3). The LC analysis of a surface water sample spiked at this low level is shown in Fig. 5, in which the chromatogram was obtained by means of blank subtraction. Three different water matrices (ground, surface and drinking water, $n = 2$ for each sample type) spiked at 1 μg/l were analysed on different days. As indicated in Table 2, the corresponding recovery and reproducibility ($n = 6$) of these experiments was 97% and 10%, respectively.

The rapid precolumn derivatization procedure (see Experimental) and the short time of the subsequent LC analysis result in a sample throughput of at least 50 per day. The method appears to be very robust. During the time of experiments (3 months of daily use), the $C_{18}$ column (C-1) maintained its performance and readjustment of column-switching conditions was

Table 2
Recoveries and relative standard deviations (R.S.D.) for environmental water samples spiked at different levels with glufosinate

| Spiked level (μg/l) | Recovery (%) | R.S.D. (%) |
|---|---|---|
| 5[a] | 100 | 2.1 |
| 0.5[a] | 95 | 2.0 |
| 0.25[a] | 118 | 11 |
| 1[b] | 97 | 10 |
| 0.1[c] | 78 | 12 |

[a] Surface water ($n = 5$).
[b] Surface water ($n = 2$), ground water ($n = 2$) and drinking water ($n = 2$), analysed on different days.
[c] Ground water ($n = 5$); values obtained after fivefold preconcentration of water sample.

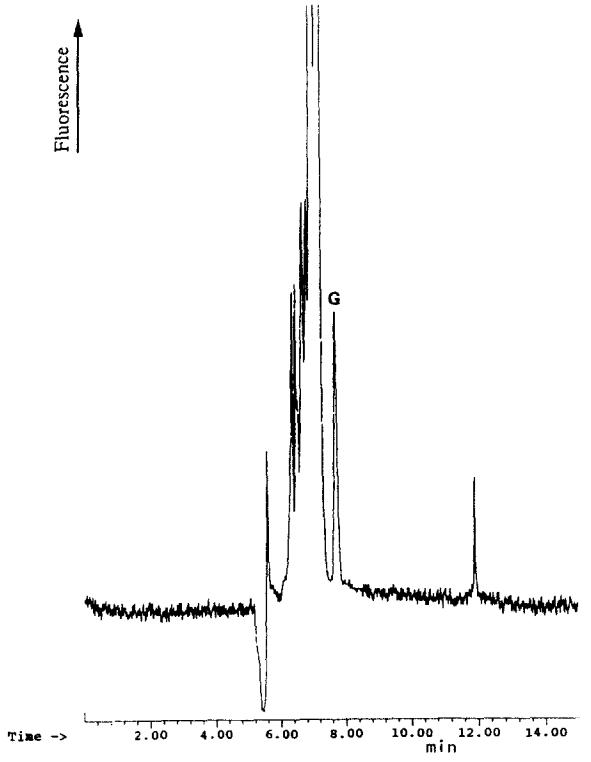



Fig. 4. Column-switching LC–FD with large-volume (2.0 ml) injection of a surface water sample containing 1.0 $\mu$g/l of glufosinate. (For LC conditions, see Experimental).

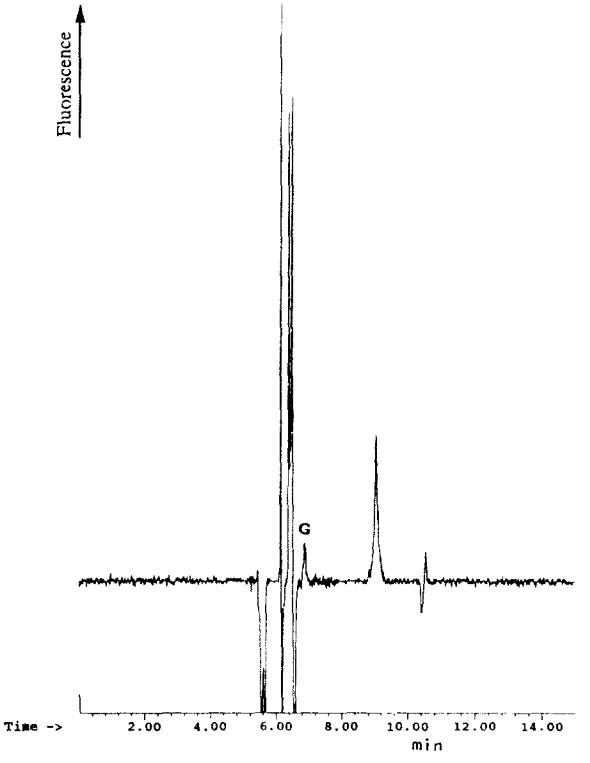



Fig. 5. Column-switching LC–FD of a surface water sample spiked with glufosinate at the 0.25 $\mu$g/l level. Chromatogram obtained after blank subtraction. LC conditions as in Fig. 4.

not necessary. The amino column (C-2) suffered a gradual decrease in efficiency only noticeable after 2 months of use.

The possibility of lowering the limit of detection to 0.1 $\mu$g/l by simply concentrating a certain volume of water sample prior to derivatization was investigated. A fivefold decrease in sample volume by means of a Rotovapor (see Experimental) was sufficient to determine glufosinate in groundwater down to a level of 0.1 $\mu$g/l. Fig. 6 shows a chromatogram for a surface sample spiked at 0.1 $\mu$g/l and concentrated fivefold. The recovery and repeatability ($n = 5$) at this level were 78% and 12% (relative standard deviation), respectively.

## 5. Conclusions

The combination of precolumn FMOC derivatization and coupled-column LC with fluorescence detection appears to be a viable approach for the rapid determination of glufosinate in environmental water samples down to a level of 0.25 $\mu$g/l. The sample throughput of about 50 per day makes the procedure highly suitable for screening purposes. If necessary, the limit of detection can be lowered to 0.1 $\mu$g/l by means of a simple preconcentration step.

## Acknowledgements

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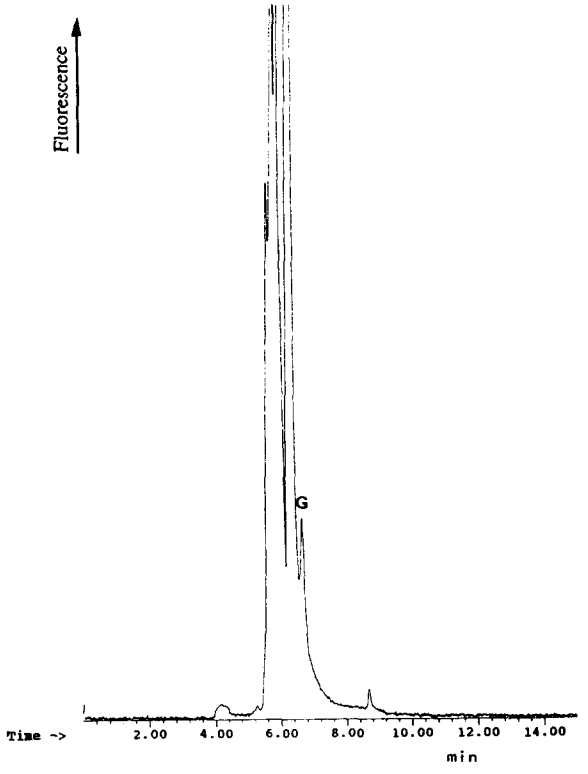


Fig. 6. Column-switching LC–FD of a fivefold concentrated surface water sample spiked with glufosinate at the 0.1 μg/l level. LC conditions as in Fig. 4.

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