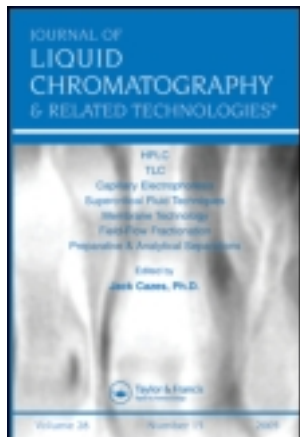


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## Analysis of Acidic Herbicides in Water Using a Toroidal Coil CCC

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### ABSTRACT

A newly developed compact toroidal coil centrifuge chromatograph (TCCC) has been proven to be able to achieve high-resolution counter-current chromatography (CCC) separations. The potential of this device is studied for analytical applications. The TCCC was used for the analysis of acidic herbicides in order to reduce the interference due to humic substances. Aqueous samples were pretreated with solid-phase extraction (SPE) and eluted with the lower phase of an *n*-hexane–ethyl acetate–water (15 : 7 : 20, v/v/v) solvent system. Because the humic substances were more hydrophilic than the herbicides, they were eluted first and separated from the herbicides. Although four herbicides were well resolved, quantification of compound 2,4-dichloro-phenoxyacetic acid was, to some extent, affected by the tailing signal of humic substances. Samples of analytes of 20 µg/L spiked in deionized water containing 6 and 12 mg/L humic acid, and in lake water,

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were analyzed. Mean recoveries ranged between 66 and 96%, with RSDs between 2 and 11%. While CCC has been known as a preparative chromatographic technique, the potential of using a TCCC device for quantitative analysis under complex matrices is demonstrated.

*Key Words:* Toroidal coil centrifuge; Countercurrent chromatography; Acidic herbicides; Humic substances.

## INTRODUCTION

Counter-current chromatography (CCC) has been developed as an efficient technique for preparative separations due to its high volume proportion of stationary phase retained in the column.<sup>[1,2]</sup> Without needing porous solid-state support to retain the stationary phase in the CCC column, persistent adsorption would not happen during separations; that results in high sample recovery. Separation is merely attributable to partitioning of analytes between the stationary and mobile phases. The solvent system, i.e., the stationary and mobile phases, is usually prepared by thoroughly mixing two or multi-component liquids. In addition to the conventional CCC, Weisz et al. has developed a technique called pH-peak-focusing, and a closely related technique called pH-zone-refining;<sup>[3,4]</sup> by subtle manipulation of solvent system pH, the sample size can be greatly increased without changing the instrument configuration. Accordingly, more and more applications appear in the literature.<sup>[5-8]</sup> Furthermore, Ito et al. explored another new form of CCC, i.e., centrifugal precipitation chromatography, which can be used to fractionate proteins using a gradient of salt.<sup>[9-11]</sup> These new discoveries have enriched the researches and applications in CCC.

In addition to applications in preparative separations, a recently developed toroidal coil rotating assembly<sup>[12]</sup> demonstrated great potential to perform analytical separations, especially for biological samples, which tend to produce emulsification in the high-speed CCC. With a relatively smaller column volume (typically about 10 mL), its separation efficiency could reach 10,000 theoretical plates at very low mobile phase flow rates. However, applications for quantitative analysis have not been found in the literature. For low- or non-volatile samples, a high performance liquid chromatography (HPLC) would be a suitable choice due to its high efficiency. While analyzing samples in complicated matrices, there may be matrix interferences to the analytes. Furthermore, matrix molecules may adsorb to the solid-state packing material and cause permanent damage to the HPLC columns. Without solid-state packing, CCC may be a good tool for separating samples in complicated matrices.





Analysis of acidic herbicides in water is usually done using HPLC. Pre-concentration by extraction is carried out in order to increase the detection sensitivity and lower the matrix interferences. Due to its high efficiency and solvent saving, solid-phase extraction (SPE) or solid-phase microextraction (SPME) is usually preferable to liquid-liquid extraction. However, a broad hump<sup>[13-16]</sup> due to co-extracted humic substances in water matrix usually appears and causes severe baseline deviation in the chromatograms when using a UV detector to monitor the effluent. Humic substances are a group of complex compounds with a wide range of molecular weights and distributed widely in soil, sediment, and natural waters.<sup>[17,18]</sup> The annoying signals would affect accurate quantification of these compounds. Water samples are usually adjusted to lower pH in order to extract the target compounds, i.e., acidic herbicides, using C18 SPE cartridges. Ionization of humic substances with the presence of phenolic and carboxylic functional groups is suppressed under lower pH values, and unavoidably co-extracted with the target components. In addition to interfering in quantification, the signal hump actually represents a great amount of unwanted substances in the sample that may shorten the column lifetime due to permanent adsorption. Accordingly, several techniques have been developed in order to remove the humic acid interferences.<sup>[19-22]</sup> The use of restricted access media (RAM) columns has also drawn attention.<sup>[23-25]</sup> Since the target compounds are all small molecules and the humic substances are relatively large molecules, a RAM column seems a good device to retain humic substances, while letting the acidic herbicides go through. Recently, a comprehensive investigation was accomplished to provide the strategies in using analytical RAM columns in removing the humic acid interferences during the determination of acidic herbicides.<sup>[26]</sup> Although, signal humps due to humic substances were still observed using UV detection, the interferences were greatly reduced, therefore, detection limits were significantly lowered.

In this study, the quantitative determination of acidic herbicides in water with the presence of humic substances was examined as an example to demonstrate the potential applications of CCC in complex matrices.

## EXPERIMENTAL

### Chemicals

2,4-Dichloro-phenoxyacetic acid (2,4-D) (>95%), 2-(2,4-dichlorophenoxy)-propanoic acid (2,4-DP) (>95%) and 4-chloro-2-methyl-phenoxyacetic acid (MCPA) (95-97%) were purchased from Sigma (St. Louis, MO), while 2-(4-chloro-2-methyl-phenoxy) propionic acid (MCPP) (95%) was from





Lancaster (Eastgate, UK). The chemical structure,  $pK_a$ , and the maximum absorption wavelength of the herbicides are listed in Table 1. Stock solutions (500  $\mu\text{g/mL}$ ) of the herbicides were prepared in mobile phase. Humic acid (Lot and Filling Code 45729/1 24300) was obtained from Fluka (Buchs, Switzerland). HPLC grade *n*-hexane, ethyl acetate, methanol, and acetone were obtained from TEDIA (Fairfield, Ohio), and deionized water from Milli-Q plus (Bedford, MA).

**Table 1.** Information on herbicides analyzed in this study.

Name	Structure	$pK_a$	$\lambda_{\text{max}}$ (nm)	$K_D^a$
2,4-Dichloro-phenoxyacetic acid (2,4-D)		2.64	203	3.4
4-Chloro-2-methyl-phenxyacetic acid (MCPA)		3.07	202	5.3
2-(2,4-Dichlorophenoxy)-propanoic acid (2,4-DP)		2.86	204	7.6
2-(4-Chloro-2-methyl-phenoxy) propionic acid (MCPA)		3.78	202	15

<sup>a</sup> $K_D$  is the solute distribution coefficient calculated using the chromatogram in Fig. 1.





### Solid-Phase Extraction Process

C18 cartridges (500 mg, 6 mL; purchased from Supelco) were pretreated with one portion of 3 mL methanol, one portion of 3 mL acetone, and followed by another portion of 3 mL methanol. Passing 6-mL water of pH 2.2 then acidified the cartridges. A 500-mL water sample added with humic acid (3 or 6 mg, equivalent to 6 or 12 mg/L of the solution) was also acidified to pH 2.2 with hydrochloric acid. Since un-dissolved powders were observed, the aqueous solution was filtered using a 0.45  $\mu\text{m}$  filter paper to remove the powders, and then percolated through the cartridge with a flow of about 4 mL/min. The cartridge was dried by passing air for 30 min, and eluted with 3 mL of methanol and 3 mL of acetone. The collected extract was evaporated to dryness using a water bath. The residue was dissolved in 1 mL of the lower aqueous phase for the subsequent CCC analysis.

### Countercurrent Chromatographic Analysis

A toroidal coil centrifuge was purchased from Pharma-Tech Research Corp, Baltimore, MD. The column was prepared from a 44 m long PTFE (polytetrafluoroethylene) tubing of 0.4 mm I.D. that was wound around a nylon pipe of 1.5 mm O.D. making about 8800 turns. The total capacity measures about 5.8 mL. The inlet and outlet tubings were 0.35 mm I.D. thick wall PTFE tubings in order to survive the constant anti-twisting motion. The detailed description can be found elsewhere.<sup>[12]</sup>

A solvent system composed of *n*-hexane–ethyl acetate–water (15 : 7 : 20, v/v/v) was prepared in a separatory funnel. Through thorough mixing, the two phases were separated after equilibrium. The standard sample solutions were prepared by dissolving individual samples in lower phase. During the separation, the toroidal coil was first filled with the stationary phase (the upper phase). The mobile phase was then pumped into the column while the column was rotating at 1500 rpm. Sample solutions (20  $\mu\text{L}$ ) were injected into the column through a Rheodyne 6-port-valve. The effluent was monitored at 280 nm using a Bio-Rad (Hercules, CA) Model 1801 UV–vis detector, and the signal was analyzed using a SISC Chem. Lab Data Station (Taipei, Taiwan).

During the search for a suitable solvent system, the analyte partition coefficient between the upper and the lower phases was measured. The solvent system was prepared by mixing desired components in a separatory funnel. 0.01 g of individual herbicide was weighed out and added to 10 mL upper and lower phases. 0.01 mL of the upper and lower phases were withdrawn and diluted to 5 mL methanol. The absorbances of both solutions were measured





with an Agilent Technologies Model 8453 (Waldbronn, Germany) spectrophotometer to estimate the partition coefficient of the component.

## RESULTS AND DISCUSSION

### Search for the Solvent System

Due to the relatively high polarity of the target components, the first attempt was to try the solvent system of *n*-hexane–ethyl acetate–methanol–water (1 : 1 : 1 : 1, v/v/v/v). After examining different compositions, it was found that methanol was not necessary. The solvent system of *n*-hexane–ethyl acetate–water (3 : 1 : 4, v/v/v) demonstrated the ability to separate the mixture. By increasing the polarity of the stationary phase with a higher ratio of ethyl acetate, the separation was optimized to reach baseline resolution by a composition of *n*-hexane–ethyl acetate–water (15 : 7 : 20, v/v/v). Although, the separation efficiency may reach a level close to that of HPLC at a very slow flow rate such as 0.01 mL/min according to literature,<sup>[12]</sup> a 20 times higher flow rate (0.2 mL/min) was chosen in this work to reduce separation time, which means that baseline resolution is not quite reached.

### Detection

Absorption spectra were measured for four herbicides. The absorbance maxima all appeared close to 200 nm. Unfortunately, due to strong absorption of ethyl acetate in this region ( $\lambda_{\text{max}}$  at about 215 nm), the monitoring wavelength for the effluent was set at 280 nm, at which the absorbances of the analytes were about one order of magnitude lower than that at 200 nm.

### Calibration

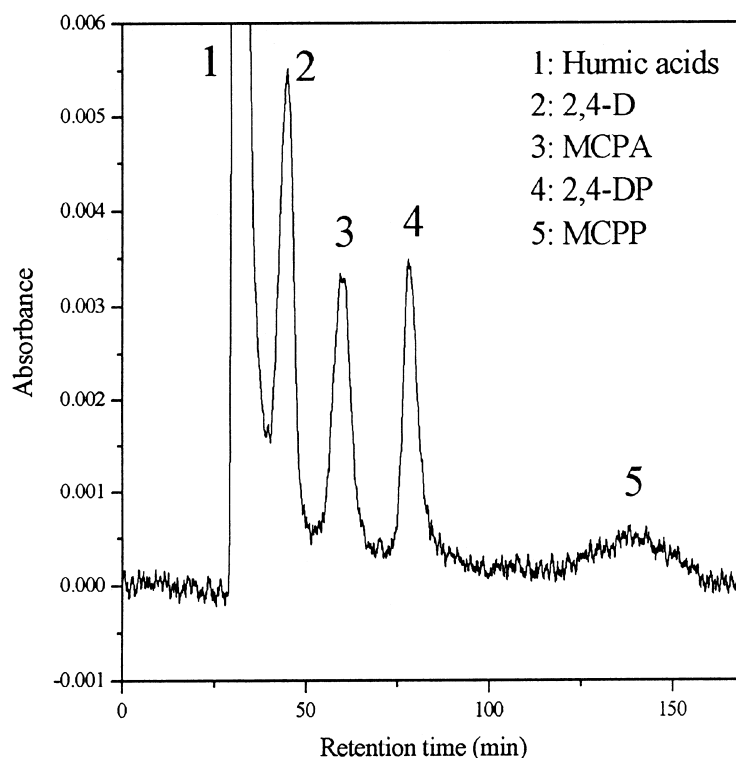
Standard solutions of 5, 10, 20, 30, 50, and 100 mg/L were made from diluting stock solution with mobile phase. Standard samples were injected into the toroidal CCC individually. All four calibration curves (peak area vs. concentration) gave linear regression coefficients greater than 0.999. Calibration using peak area gave better results than using peak height because the peak area remains the same even when phase depletion occurred.





### Measurements with Spiked Samples and Real Waters

Sample solutions containing four herbicides (20  $\mu\text{g}/\text{mL}$  each), were prepared by adding humic acid of 6  $\mu\text{g}/\text{mL}$ . Samples were treated with SPE and then injected into CCC. The chromatogram is shown in Fig. 1. The distribution coefficients of the four solutes are listed in Table 1. Although the signal of humic acid was much greater than those of the analytes, it was separated from the analytes. A chromatogram (not shown) of a sample containing humic acid alone showed a peak tailing off very rapidly and



**Figure 1.** Chromatogram of four herbicides (20  $\mu\text{g}/\text{L}$ ) in a water matrix containing 6  $\mu\text{g}/\text{mL}$  humic acid. The sample solution was prepared in 500 mL deionized water and acidified to pH 2.2. After SPE treatment, an aliquot of 20  $\mu\text{L}$  from the final 1 mL total sample volume was injected to the toroidal coil CCC. The operational parameters for the TCCC: column volume 5.8 mL; stationary phase retention 1.6 mL, phase retention ratio = 27.5%; centrifuge rotation speed 1500 rpm; solvent system *n*-hexane–ethyl acetate–water (15 : 7 : 20, v/v/v); monitoring wavelength 280 nm.

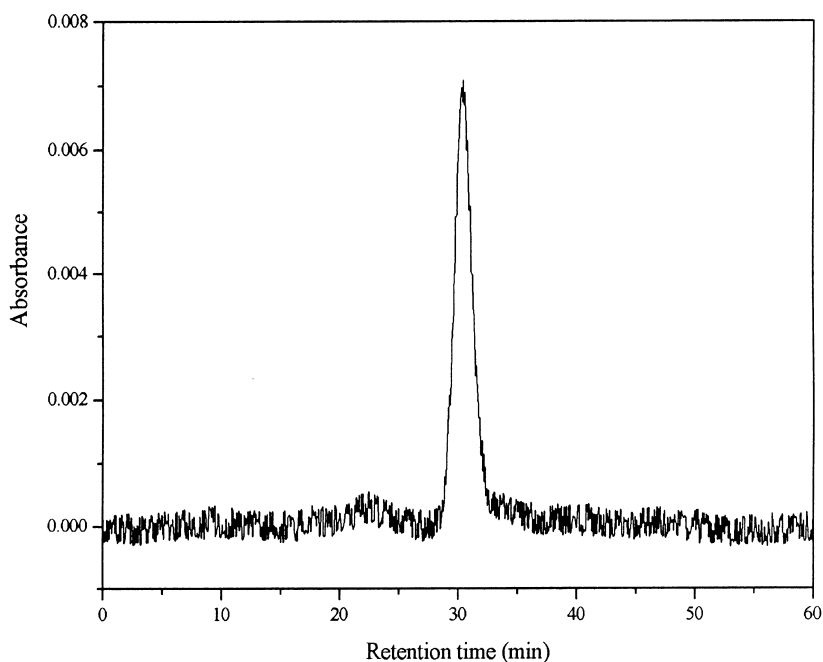






smoothly into where the analytes were expected to appear; that ensured good accuracy of acquiring analyte peak areas.

In addition to de-ionized water, water fetched from the Bamboo Lake at the Chiao Tung University was also used to prepare sample solutions. The standard SPE procedure was executed to examine the water from the Bamboo Lake. A large signal appeared at the retention time where the humic acid was expected, while the four herbicides were not detectable. A few water samples taken from the Bamboo Lake on different days were examined. The humic acid signal was found relatively greater after it rained. However, the signal intensities all emerged between those brought about by 6 and 12 mg/L humic acid. The lake water samples were directly injected into the toroidal coil centrifuge chromatograph (TCCC) several times, without any pre-treatment. Signals appeared at the same retention time as that of the sample treated with SPE, only the signal magnitudes were much smaller (Fig. 2). This examination, again, proves the capability of CCC to cope with samples of complex matrices.



**Figure 2.** Chromatogram of water sample taken from Lake Bamboo at the National Chiao Tung University. Twenty microliter water was injected to the TCCC without any pre-treatment. The experimental parameters were essentially same as described in Fig. 1.





**Table 2.** Mean recoveries ( $n = 3$ ) and RSDs of the herbicides at 20  $\mu\text{g/L}$  in different water matrixes.

Matrix	Herbicide mean recoveries (RSD, %)			
	2,4-D	MCPA	2,4-DP	MCPP
De-ionized water	96(7)	74(2)	88(3)	78(4)
De-ionized water with 6 mg/L humic acid	89(2)	75(2)	88(2)	75(4)
De-ionized water with 12 mg/L humic acid	85(11)	66(9)	84(7)	77(11)
Lake water	89(3)	75(4)	85(6)	82(5)

To ensure the potential of using toroidal CCC for quantitative analysis under the matrix of humic substances, water samples in different matrixes were analyzed. Herbicide samples (20  $\mu\text{g/L}$  for each) were doped with either 6 or 12 mg/L humic acid and treated with the SPE process. The results (see Table 2) have shown reasonably good recovery and reproducibility. The matrix containing higher concentration of humic acids affected the measurement repeatability the most. To examine the cause for the recovery lower than 100%, a sample solution containing 15 mg/L of each four herbicides, and 30 mg/L of the humic acid, was prepared and separated, directly, without conducting the SPE process. The recovery for all four compounds essentially all reached the 100% level. Thus, the main reason responsible for the lower recovery may result only from the SPE process. The non-specific adsorption of SPE processes can be a real problem, which CCC can avoid.

## CONCLUSIONS

Toroidal coil centrifuge chromatograph is able to successfully separate a mixture of four herbicides in a complex matrix of humic acid. For quantitative determinations, the samples were first treated with solid-phase extraction. Due to the hydrophilic origin of the humic substances, the matrix peak appeared before all analyte peaks. The peak tailing was found not to significantly affect quantification of the analytes. The signal humps, due to humic substances regularly observed in HPLC separations, did not appear in CCC separations. No column damage or clogging happened even with injecting several lake water samples directly into the column without filtration. Since the separation efficiency of toroidal CCC is not comparable to that of HPLC, it would not be able to separate more analytes in complicated mixtures. The separation





efficiency declined occasionally, due to the phase depletion during elution. Accordingly, quantitative determination using peak area would be much more repeatable than using peak height. The monitoring wavelength of the analytes was not positioned at their absorption maxima because of the interference from ethyl acetate in the mobile phase. The sensitivity should increase by an order of magnitude without this interference. Although it took about 2 h to accomplish one chromatographic experiment in our study, the analysis time could be greatly reduced using other CCC devices, such as the small coil J type CCC centrifuge<sup>[27]</sup> developed recently. In conclusion, we demonstrated in this study the potential of using toroidal coil CCC for quantitative analysis in a complicated matrix.

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#### REFERENCES

1. Mandava, N.B.; Ito, Y. Eds. *Countercurrent Chromatography: Theory and Practice*; Marcel Dekker, Inc.: New York, 1988.
2. Conway, W.D. *Countercurrent Chromatography: Apparatus, Theory, and Applications*; VCH Publishers: New York, 1989.
3. Weisz, A.; Scher, A.L.; Shinomiya, K.; Fales, H.M.; Ito, Y. A new preparativescale purification technique—pH-zone-refining countercurrent chromatography. *J. Am. Chem. Soc.* **1994**, *116*, 704–708.
4. Weisz, A.; Scher, A.L.; Ito, Y. Isolation of 4-bromo-4,5,6,7-tetrachloro-fluorescein from a synthetic mixture by pH-zone-refining counter-current chromatography with continuous pH monitoring. *J. Chromatogr. A.* **1996**, *732*, 283–290.
5. Pennanec, R.; Viron, C.; Blanchard, S.; Lafosse, M. Original uses of the pH-zone refining principle: adaptation to synthesis imperatives and to ionic compounds. *J. Liq. Chromatogr. & Rel. Technol.* **2001**, *24*, 1575–1591.
6. Chadwick, L.R.; Wu, C.D.; Kinghorn, A.D. Isolation of alkaloids from goldenseal (*Hydrastis canadensis* rhizomes) using pH-zone refining countercurrent chromatography. *J. Liq. Chromatogr. Rel. Technol.* **2001**, *24*, 2445–2453.





7. Kitazume, E.; Higashiyama, T.; Sato, N.; Kanetomo, M.; Tajima, T.; Kobayashi, S.; Ito, Y. On-line microextraction of metal traces for subsequent determination by plasma atomic emission spectrometry using pH peak focusing countercurrent chromatography. *Anal. Chem.* **1999**, *71*, 5515–5521.
8. Yang, F.; Quan, J.; Zhang, T.; Ito, Y. Preparative separation of alkaloids from the root of *Sophora flavescens* Ait by pH-zone-refining countercurrent chromatography. *J. Chromatogr. A* **1998**, *822*, 316–320.
9. Ito, Y. Centrifugal precipitation chromatography: principle, apparatus, and optimization of key parameters for protein fractionation by ammonium sulfate precipitation. *Anal. Biochem.* **2000**, *277*, 143–153.
10. Sookkummerd, T.; Hsu, J.T.; Ito, Y. Purification of PEG-protein conjugates by centrifugal precipitation chromatography. *J. Liq. Chromatogr. Rel. Technol.* **2000**, *23*, 1973–1979.
11. Ito, Y. Centrifugal precipitation chromatography applied to fractionation of proteins with ammonium sulfate. *J. Liq. Chromatogr. Rel. Technol.* **1999**, *22*, 2825–2836.
12. Matsuda, K.; Matsuda, S.; Ito, Y. Toroidal coil counter-current chromatography—achievement of high resolution by optimizing flow-rate, rotation speed, sample volume and tube length. *J. Chromatogr. A* **1998**, *808*, 95–104.
13. Di Corcia, A.; Marchetti, M. Multiresidue method for pesticides in drinking-water using a graphitized carbon-black cartridge extraction and liquid chromatographic analysis. *Anal. Chem.* **1991**, *63*, 580–585.
14. Pichon, V.; Cau Dit Coumes, C.; Chen, L.; Guenu, S.; Hennion, M.C. Simple removal of humic and fulvic acid interferences using polymeric sorbents for the simultaneous solid-phase extraction of polar acidic, neutral and basic pesticides. *J. Chromatogr. A* **1996**, *737*, 25–33.
15. Coquart, V.; Hennion, M.C. Determination of phenoxyacid herbicides in drinking-water at the Ppt-level by liquid chromatography and online selective preconcentration. *Sci. Total Environ.* **1993**, *132*, 349–360.
16. Masque, N.; Galia, M.; Marce, R.M.; Borrull, F. New chemically modified polymeric resin for solid-phase extraction of pesticides and phenolic compounds from water. *J. Chromatogr. A* **1998**, *803*, 147–155.
17. Aiken, G.R.; McKnight, D.M.; Wershaw, R.L.; MacCarthy, P. Eds. *Humic Substances in Soil, Sediment and Water*; Wiley: New York, 1985.
18. Gaffney, J.S.; Marley, N.A.; Clark, S.B. Eds. *Humic and Fulvic Acids/ Isolation, Structure, and Environmental Role*; ACS Symposium Series 651; American Chemical Society: Washington, D.C.: 1996.
19. Di Corcia, A.; Marchese, S.; Samperi, R. Evaluation of graphitized carbon-black as a selective adsorbent for extracting acidic organic-compounds from water. *J. Chromatogr.* **1993**, *642*, 163–174.





20. de Ruiter, C.; Minnaard, W.A.; Lingeman, H.; Kirk, E.M.; Brinkman, U.A.T.; Otten, R.R. Sensitive and selective fluorescence detection of phenoxyacid herbicides by liquid chromatography with online ion-pair extraction. *Int. Environ. Anal. Chem.* **1991**, *43*, 79–90.
21. Geerdink, R.B.; Tol-Wildenburg van, S.; Niessen, W.M.A.; Brinkman, U.A.T. Determination of phenoxy acid herbicides from aqueous samples by improved clean-up on polymeric pre-columns at high pH. *Analyst* **1997**, *122*, 889–893.
22. Nilve, G.; Audnunson, G.; Jonsson, J.A. Sample preparation by means of a supported liquid membrane for the determination of chlorophenoxy-alkanoic acids. *J. Chromatogr.* **1989**, *471*, 151–160.
23. Pinkerton, T.C. High-performance liquid chromatography packing materials for the analysis of small molecules in biological matrices by direct injection. *J. Chromatogr.* **1991**, *544*, 13–23.
24. Sancho-Llopis, J.V.; Hernandez-Hernandez, F.; Hogendoorn, E.A.; Zoonen van, P. Rapid method for the determination of 8 chlorophenoxy acid residues in environmental water samples using off-line solid phase extraction and online selective precolumn switching. *Anal. Chim. Acta* **1993**, *283*, 287–296.
25. Onnerfjord, P.; Barcelo, D.; Emneus, J.; Gorton, L.; Marko-Varga, G. On-line solid-phase extraction in liquid chromatography using restricted access pre-columns for the analysis of s-triazines in humic-containing waters. *J. Chromatogr. A* **1996**, *737*, 35–45.
26. Hogendoorn, E.A.; Dijkman, E.; Baumann, B.; Hidalgo, C.; Sancho, J.V. Strategies in using analytical restricted access media columns for the removal of humic acid interferences in the trace analysis of acidic herbicides in water samples by coupled column liquid chromatography with UV detection. *F. Hernandez Anal. Chem.* **1999**, *71*, 1111–1118.
27. Janaway, L.; Hawes, D.; Wood, P.; Sutherland, I. *A New Rapid Analytical Countercurrent Chromatography: The Description of a Rapid, Small Coil Volume CCC Instrument Capable of Directly Interfacing with a Mass Spectrometer Detector*, 2nd International Conference on Counter-Current Chromatography, Beijing, April 15–20, 2002; 45.

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