Extraction and determination of the Mitins sulcofuron and flucofuron from environmental river water

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Flucofuron and sulcofuron, both examples of Mitins, were employed as the active ingredients in mothproofing formulations for the protection of textile fabrics by the dyeing industry. Monitoring of their presence in components of the river ecosystem is a regulatory requirement so precise extraction techniques, combined with sensitive detection systems, are required to obtain valid data concerning the levels of target pollutants present. This study continued the development of liquid chromatography combined with negative-ion electrospray ionization tandem mass spectrometry (LC–ESI-MS–MS) operated in the multiple reaction monitoring mode for the determination of these analytes in complex matrices. The paper describes the development of liquid–liquid extraction (LLE) and solid-phase extraction (SPE) techniques for the determination of the analytes in environmental river water. The methods employed an internal standard, trichlorocarbanilide (TCC), to check the extraction efficiencies but not to correct environmental data. The extraction efficiencies obtained with LLE were 73.2 ± 6.7, 112.4 ± 8.6 and 96.4 ± 14.3% (n = 5) compared with 74.3 ± 8.4, 115.9 ± 3.1 and 112.7 ± 4.5% (n = 4) employing SPE for sulcofuron, flucofuron and TCC (100 ng l^{-1} matrix fortification level), respectively. The SPE results are consistent with those obtained for LLE, although the precision of the SPE method was better than that of the LLE method. These methods were then successfully applied to samples obtained from a contaminated ecosystem.

Keywords: *Mitins; sulcofuron; flucofuron; mothproofing agents; environmental river water; liquid–liquid extraction; solid-phase extraction; liquid chromatography–electrospray ionization tandem mass spectrometry*

The pattern of mothproofing agent use has altered considerably since the end of the 1970s. The discovery that dieldrin was highly toxic to mammals and very persistent in the environment led to a decline in its use and replacement by formulations based on substituted ureas, commonly grouped under the term urons.

The term mothproofing describes the treatment of wool or wool-based fabrics to prevent damage by the larvae of a number of insect pests[1,2] that are capable of digesting keratin. Each mothproofing formulation contains an active ingredient, or combination of active ingredients, solvent, surfactant and water. Sulcofuron and flucofuron, both examples of urons, exert their toxic effect on the target organism by inhibiting the synthesis of the enzyme required to break down keratin.[1]

Mothproofing agents form chemical bonds with wool fibres in the same way as dyes and, therefore, the preferred method of application is during the dyeing process. The requirements for an active ingredient are restrictive, and consequently few general formulations are suitable for mothproofing. For example, in addition to being toxic to the insects at low levels of application, it must be stable to the application conditions, resistant to washing and light and effective for prolonged periods on the textile.[2]

Mitin is the registered tradename for mothproofing agents produced by Ciba-Geigy (Basle, Switzerland). Mothproofing agents previously marketed in the UK include Mitin FF High Conc containing sulcofuron (80%) and Mitin LP containing flucofuron (7.6%).[1]

Regulations designed to prevent the pollution of surface waters by sulcofuron and flucofuron were implemented in the UK on January 1, 1993.[3] Contamination of freshwater ecosystems by sulcofuron and flucofuron occurs directly owing to the discharge of industrial effluents or indirectly through the discharge from sewage treatment works. In tests involving activated sewage sludge, both analytes were strongly adsorbed on particulate matter, so it is therefore not unreasonable to suggest that they are persistent in the environment.[1] The environmental quality standards (EQSs) for sulcofuron and flucofuron in fresh water required to support fish are 25.0 and 1.0 μg l^{-1}, respectively.[1,3]

In this paper, the reported use of liquid chromatography combined with negative-ion electrospray ionization tandem mass spectrometry (LC–ESI-MS–MS) for the determination of sulcofuron and flucofuron is continued.[4] We describe the development of liquid–liquid extraction (LLE) and solid-phase extraction (SPE) techniques for the determination of the analytes in environmental surface waters. The methods employ an internal standard, trichlorocarbanilide (TCC), to check the extraction efficiencies. The methods reported were successfully applied to samples obtained from a contaminated ecosystem.

Experimental

Sulcofuron {sodium 5-chloro-2-[4-chloro-2-(3,4-dichlorophenyl)ureido]phenoxybenzenesulfonate} [3567-25-7] was obtained from Ciba-Geigy (Macclesfield, Cheshire, UK), flucofuron [1,3-bis(4-chloro-α,α,α-trifluoro-*m*-tolyl)urea] [370-50-3] was custom synthesized at the University of Salford, from 4-chloro-3-(trifluoromethyl)phenyl isocyanate [16588-69-5] and 5-amino-2-chlorobenzotrifluoride [320-51-4],[5] and TCC [1-(4-chlorophenyl)-3-(3,4-dichlorophenyl)urea] [101-20-2], the internal standard, was purchased from Aldrich (Gillingham, Dorset, UK). HPLC grade dichloromethane and methanol and analytical-reagent grade acetone, ethyl acetate and anhydrous sodium sulfate were all obtained from Fisons (Loughborough, UK). The variety of solid-phase cartridges were purchased from Jones Chromatography (Hengoed, Mid-Glamorgan, UK).

The eluent was delivered by an isocratic system employing a Gilson Model 302 HPLC pump (Anachem, Luton, UK). LC separations were performed using a C_8/C_{18} silica fully end-capped HiChrom HiRPB column (250 × 2.1 mm id, 5 μm particle size) (HiChrom, Reading, Berkshire, UK) with methanol-water (9 + 1 v/ v) as the mobile phase at a flow rate of 0.2 cm^3 min^{-1}. Samples were introduced on to the column employing manual injection into a six-port Rheodyne (Cotati, CA, USA) Model 7125, injector fitted with a 20 μl loop.

The LC system was connected to a VG Quattro mass spectrometer (VG Biotech, Manchester, UK) equipped with a

Megaflow electrospray probe and operated in the negative-ion mode. After separation, the sample flow was split so that 25% of the injection volume entered the source through a 150 cm × 100 μm id fused-silica capillary line (SGE, Milton Keynes, UK) together with nitrogen nebulizing gas (CP grade) (Air Products, Walton-on-Thames, UK) which flowed coaxially through the probe tip at 40 l h^{-1}. A nitrogen bath gas, flow rate approximately 150 l h^{-1}, was also employed to assist the desolvation process.

Mass spectra were collected in full scan (*m/z* 100–1200 in 2 s) and multiple-reaction monitoring (MRM) (dwell time = 0.1 s, span = 0.02 u) modes. The source temperature was maintained at 120 °C and the sampling cone voltage was 35 V. MRM was performed while employing argon gas (CP grade, Air Products) in the collision cell at a nominal pressure (1.0×10^{-4} mbar) set to induce a 50% reduction in the precursor ion intensity. The collision energy was 70 eV. Instrument control and data processing included the use of the supplied VG MassLynx 2.1 application software.

Stock standard solutions of the reference compounds for long-term storage were prepared at concentrations of 100 mg l^{-1}. These solutions were serially diluted to prepare mixed working standard solutions of sulcofuron, flucofuron and TCC in the mobile phase in the required concentration range (0.5–500 μg l^{-1}). These standard solutions were analysed by LC–ESI-MS–MS operating in the MRM mode. External calibration was employed for the quantification of the analytes and the internal standard. Linearity was observed for both analytes (1–500 μg l^{-1}) with correlation coefficients of 0.999 obtained routinely. Peak areas were obtained from the mass chromatograms for the monitored reaction of each analyte and calibration curves generated from plots of peak area against analyte concentration. The instrumental limit of detection (LOD) was calculated from the analyte peak height/peak-to-peak baseline noise ratio and was defined as a 3 : 1 signal-to-noise ratio (S/N).

The procedures were developed and modified from US Environmental Protection Agency (USEPA) Method 625, Base/Neutrals and Acids,[6] and Methods for the Examination of Waters and Associated Materials[7] for analysing the target analytes in spiked and real samples. The recommended method makes use of tetraethylammonium bromide (TEAB) to induce ion-pair formation.[7] When applied to environmental matrices, this method is known to be unreliable.[8]

The spiking solutions, consisting of a mixture of sulcofuron and flucofuron in acetone (100 μg l^{-1}), were added to doubly distilled, de-ionized water for the recovery experiments, generating a matrix fortification level of 0.1 μg l^{-1}. The flask was vigorously shaken manually with frequent venting to release pressure and was then allowed to equilibrate overnight.

The contaminated samples were collected from seven sites located at Meltham (near Huddersfield), West Yorkshire, UK, a catchment of the River Calder. The region has previously been highlighted as having a concentration of industrial mothproofing agent activity amongst the highest in the world.[3] Table 1 lists the National Grid References of the seven sampling sites. Water samples were collected in glass bottles (2500 cm^3) fitted with PTFE lined caps such that a headspace was avoided. The bottles were fully immersed to collect sub-surface water. After collection, samples were transported back to the laboratory, where they were stored in the dark at 4 °C. Further processing was undertaken within 48 h of collection.

For LLE, a 1000 cm^3 aliquot of water was placed in a clean, dry separating funnel, 0.1 μg of internal standard in acetone was added into the water and the funnel was shaken vigorously to ensure homogeneity. Approximately 30 g of sodium chloride were added to the aliquot to prevent the formation of emulsions and then the solution pH was adjusted to pH 2 with the addition of 1.0 M sulfuric acid. Dichloromethane (50 cm^3) was added and the funnel was shaken vigorously for 5 min with frequent venting. When the two layers had separated sufficiently, the organic layer was drained and filtered through a sintered glass filter capped with anhydrous sodium sulfate, prepared by heating at 500 °C for 4 h, and collected in a rotary evaporation flask. The same procedure was repeated twice more with fresh dichloromethane and these extracts plus the additional rinses were combined. The volume of the solvent extracts was reduced to 0.1 μg in 5 cm^3 using a rotary evaporator under reduced pressure.

For SPE, a 1000 cm^3 aliquot of water was placed in a clean, dry glass container, 0.1 μg of internal standard in acetone was added and the container was shaken vigorously to ensure homogeneity. The 500 mg C_{18} cartridge was activated and conditioned with 5 cm^3 of acetone, followed by 5 cm^3 of methanol and 5 cm^3 of water. The sample was applied at a flow rate of approximately 10 cm^3 min^{-1}. Once the sample had passed through, the cartridge was dried for approximately 40 min. The analytes were eluted with 3 × 2 cm^3 aliquots of methanol.

The concentrated extracts from the described procedures were transferred in to a 1.0 cm^3 graduated conical vial and evaporated to less than 1 cm^3 using a gentle stream of clean, dry nitrogen gas directed on to the surface of the solvent. The vial was rinsed several times with methanol–water (9 + 1, v/v) before concentration to 0.1 μg cm^{-3}. Reconstitution of the extract in the HPLC mobile phase is reported to minimize disruption of the column equilibrium following injection and to

Table 1 National Grid References of the seven sampling sites at Meltham (near Huddersfield), West Yorkshire, a catchment of the River Calder, and the concentrations of sulcofuron and flucofuron in river water, employing LLE in October 1995 and SPE in June 1997.

		Concentration/ng l^{-1}				
		LLE		SPE		
Sampling site	National Grid Reference	Sulcofuron	Flucofuron	Sulcofuron	Flucofuron	TCC recovery (%)
Blank		N.d.*	N.d.	N.d.	N.d.	105
BDI	SE 102098	N.d	N.d.	N.d.	N.d.	107
BDII	SE 102100	N.d	N.d.	N.d.	N.d.	100
BDIII	SE 103101	4.1	N.d.	6.0	4.2	95
BR	SE 111112	2.0	1.8	6.9	4.3	102
HR	SE 110113	6.7	3.8	2.7	3.8	93
STW	SE 114117	3.1	N.d.	N.d.	4.5	99
HHB	SE 118122	8.5	N.d.	N.d.	5.7	110

* N.d. = not detected (less than the LOD).

improve the precision of the method.[9] The extracts were stored at 4 °C prior to instrumental analysis.

Results and discussion

Sulcofuron and flucofuron (Fig. 1) were selected by the National Rivers Authority (NRA) because of their history of use as textile mothproofing agents in the UK. Monitoring of their presence in environmental water is a regulatory requirement and involves reliable identification and quantification of trace levels at or below the environmental quality standards (EQSs).

The use of LC–ESI-MS–MS operated in the MRM mode has been reported previously.[4] This approach provided a highly sensitive and specific method for determining sulcofuron and flucofuron in the mid-picogram range. The instrumental LODs in the MRM mode were calculated to be 10 and 2.5 pg for sulcofuron and flucofuron, respectively.

Sulcofuron and flucofuron were extracted from doubly-distilled, de-ionized water with dichloromethane as described above without the addition of TEAB. Owing to the sulfonic acid functionality on sulcofuron, the effect of pH on extraction efficiency was investigated. This was performed by adjusting the pH of the spiked water samples at the 100 ng l^{-1} (1000 cm^3) matrix fortification level. Quantification was conducted by comparison of the analyte peak areas with those of external standards analysed in the same manner.

The results (Table 2) illustrate the suspected pH dependence of sulcofuron on the extraction efficiency from water. The best

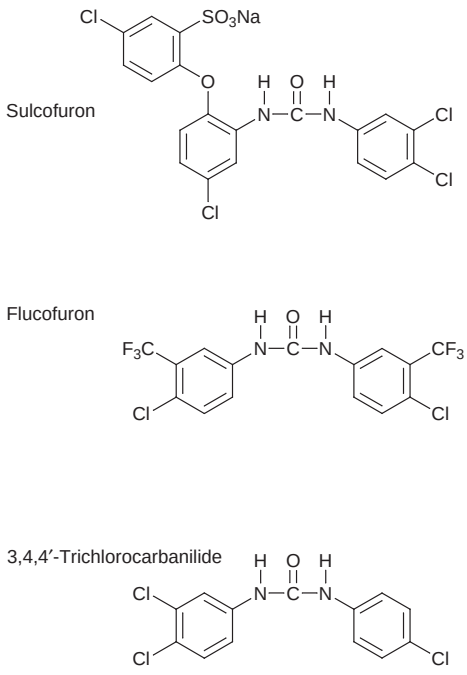

Fig. 1 Structures of flucofuron, sulcofuron and TCC.

Table 2 Dependence of LLE efficiency on water sample pH at 100 ng l^{-1} (n = 5)

	Recovery ± s (%)	
Adjusted pH	Sulcofuron	Flucofuron
Blank	N.d.*	N.d.
1	44.5 ± 5.8	42.5 ± 4.5
2	73.2 ± 6.7	112.4 ± 8.6
4	51.8 ± 8.2	117.0 ± 10.1
7	51.9 ± 16.9	114.1 ± 11.6

* N.d. = not detected (less than the LOD).

extraction efficiencies for both sulcofuron and flucofuron extracted concurrently were obtained at pH 2 and were 73.2 ± 6.7 and 112.4 ± 8.6% (n = 5), respectively.

The recovery results are consistent with those obtained for the standard method.[7] It is difficult to compare the precision of this method with that reported, as the published method reports duplicate results, whereas this study employed five replicates, in accordance with USEPA Method 625.[6] Having attained a suitable extraction procedure from doubly distilled, de-ionized water, the study moved to the more complex environmental water matrix.

Environmental water samples were collected from seven sites located at Meltham, West Yorkshire, UK (Fig. 2). The samples (1000 cm^3 aliquots) were adjusted to pH 2 and then treated identically to the spiked samples. Analysis of the extracts by negative-ion LC– ESI-MS–MS operated in the MRM mode was performed.

The results for the environmental water samples are summarized in Table 1. Sulcofuron was detected at all the active sites, in the highest concentrations at sites downstream of the sewage treatment works (STW, 6.7 ng l^{-1}) and the textile mill (BDII, 8.5 ng l^{-1}). Flucofuron was only detected at sites downstream of the sewage treatment works (STW, 3.8 ng l^{-1}, and HHB, 1.8 ng l^{-1}). These results were as expected because the most likely sources of contamination are due to the direct discharge of industrial effluents or indirectly through the outfall from sewage treatment works, where it is suggested that sulcofuron and flucofuron are accumulated by the surrounding biosphere.[1] Flucofuron was not detected at any other sampling sites. This result was considered to reflect the pattern of mothproofing agent use by the local textile industry rather than a failure of the sampling strategy, the extraction procedure or the quantitative technique employed. Flucofuron is not currently being commercially marketed in any mothproofing agents, whereas sulcofuron-based formulations are still being manufactured under the principal trade name Mitin.[10]

The BDI and HR sites were employed as control blanks and helped to confirm that the analytical method was not subject to interference, as these sites are not known to have a history of contamination and were, therefore, expected to be clean.

The levels of sulcofuron and flucofuron monitored in the environmental water samples from all the active sites were well below the EQSs of 25.0 and 1.0 μg l^{-1} for sulcofuron and flucofuron, respectively.

Having obtained a selective, sensitive, precise method for determining sulcofuron and flucofuron in river water samples, an internal standard was required to check for recovery in environmental matrices. 3,4,4′-Trichlorocarbanilide (TCC,

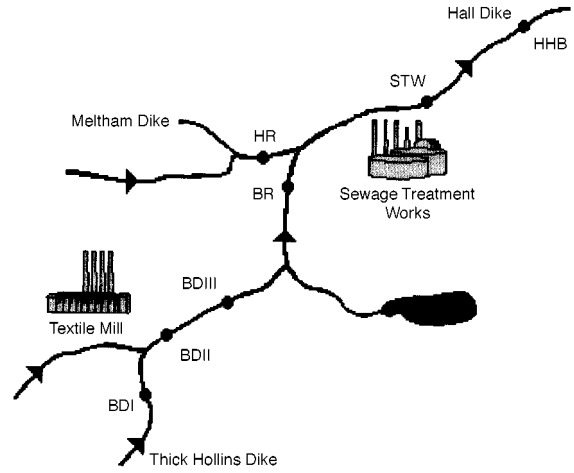

Fig. 2 Location of the seven sampling sites at Meltham, West Yorkshire, UK.

Fig. 1) was initially selected from three suitable alternatives (results not shown) on the basis of its elution proximity by reversed-phase HPLC to that of sulcofuron and flucofuron (Fig. 3) and its low probability of environmental occurrence.

A negative-ion electrospray ionization mass spectrum was collected in full scan mode for TCC (Fig. 4). Owing to the soft nature of electrospray ionization, the pseudo-molecular ion, $[M–H]^-$, is easily observed in the mass spectrum. This ion (*m*/*z* 313, 315, 317, 319) shows the correct chlorine isotope ratio (27 : 27 : 9 : 1) for the presence of three chlorine atoms. The $[M - H]^-$ ion undergoes cleavage of the nitrogen–carbon bond to give the two amines (*m*/*z* 126, 128 and *m*/*z* 160, 162, 164) after the ejection of the neutral isocyanate moieties. These fragments contain one and two chlorine atoms, as shown by the 3:1 and 9:6:1 isotope ratios, for *m*/*z* 126 and 160, respectively.

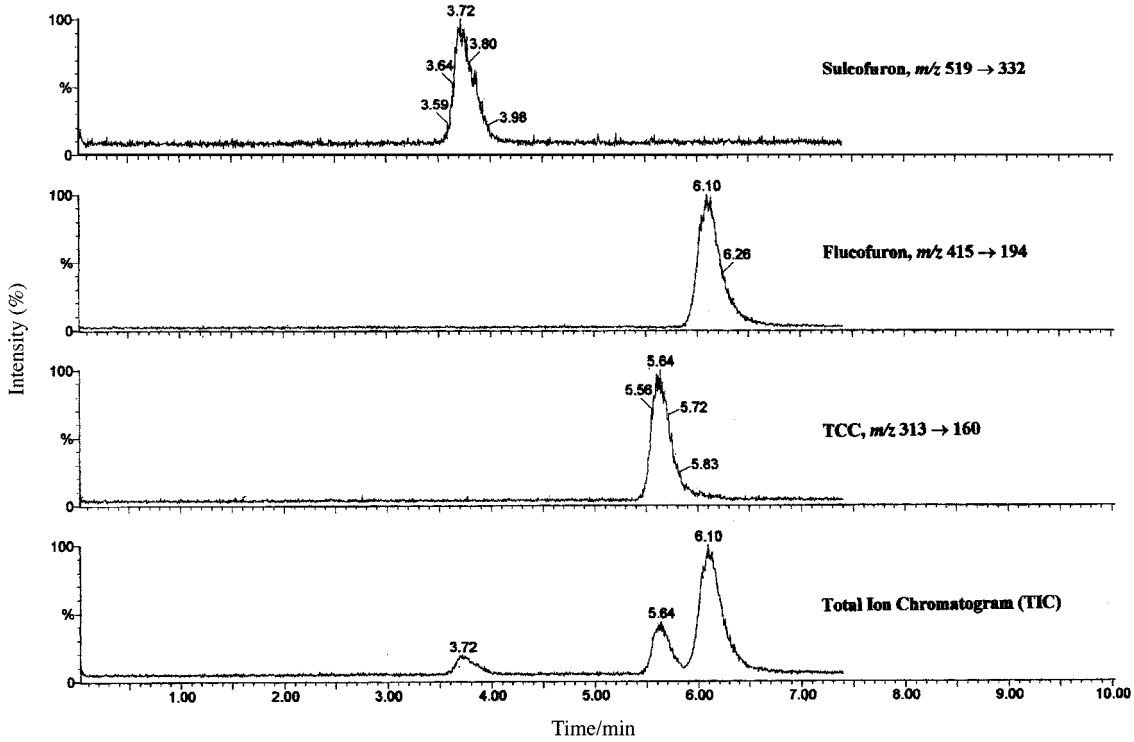

Fig. 3 Typical LC–ESI-MS–MS MRM reconstructed ion trace and TIC for sulcofuron, flucofuron and TCC after extraction, at a matrix fortification level of 100 μg l^{-1}.

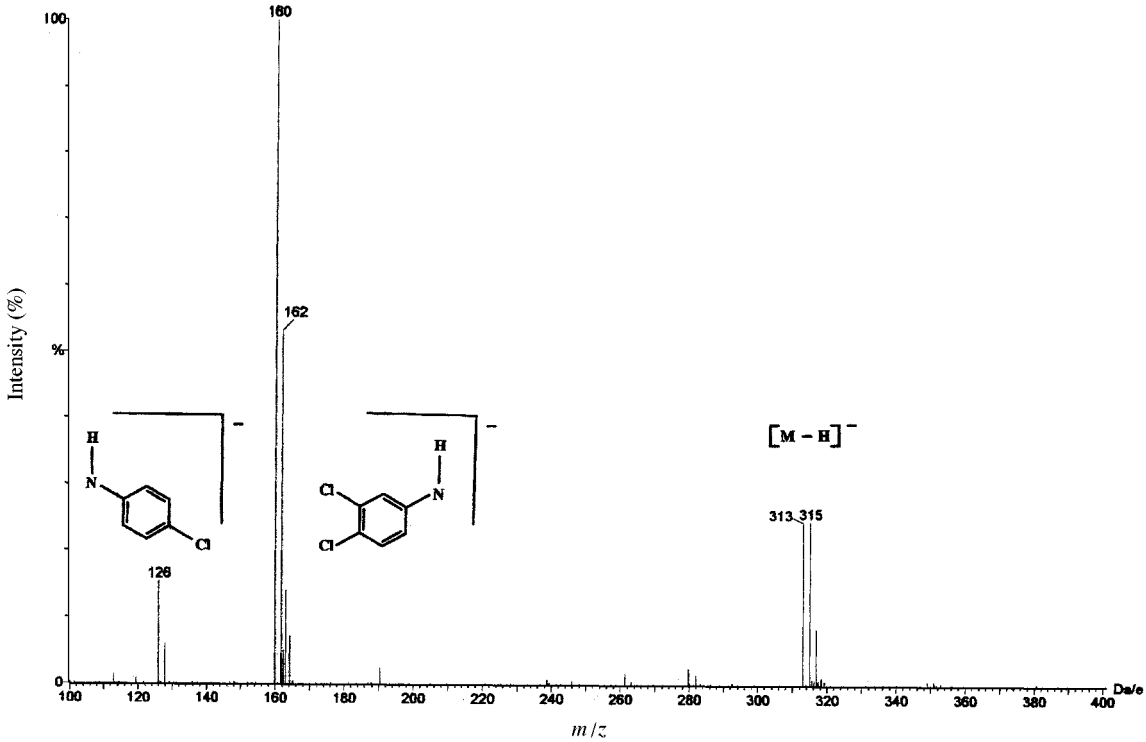

Fig. 4 Negative-ion ESI mass spectrum of TCC using a 35 V cone voltage.

A product-ion spectrum was obtained for TCC from *m/z* 313 (Fig. 5). The product-ion spectrum for TCC confirms the pseudo-molecular ion cleaving at the nitrogen–carbon bond to give the respective amines (*m/z* 160 and 126). Owing to the intensity of the product ion, *m/z* 160, compared with *m/z* 126 under these MRM conditions, the fragmentation of *m/z* 313 to give *m/z* 160 is monitored; a response at the correct retention time enables TCC to be quantified.

A typical MRM mass chromatogram obtained for sulcofuron, flucofuron and TCC at 100 μg l^{-1} (Fig. 3) illustrates that this method of detection gives a sufficiently intense response at the level of interest (mid-picogram range) for TCC. Linearity was observed for TCC (5–100 μg l^{-1}) with correlation coefficients > 0.998 obtained routinely. The absolute instrumental LOD, defined as an S/N of 3 : 1, was 3.0 μg l^{-1} for TCC.

The extraction of TCC employed methodology identical with that for sulcofuron and flucofuron. The internal standard was spiked at the 100 ng l^{-1} (1000 cm^3) matrix fortification level with pH adjustment to pH 2. The LLE efficiency from water for TCC was 96.4 ± 14.3% (n = 5). TCC was used to check the efficiencies of all subsequent methods but not to correct environmental data.

SPE is now well established in the analytical chemistry laboratory and has largely replaced classical LLE. Having developed a reliable, precise LLE method for quantifying sulcofuron and flucofuron in river water, a method was required to utilize the well documented benefits of SPE over LLE,[9,11,12] which for this application were speed, less use of solvents and reduction in costs.

Sulcofuron, flucofuron and TCC were extracted from water employing a variety of 500 mg solid phases, including octadecyl, octyl, cyclohexyl and specialty environmental phases. Once again, owing to the sulfonic acid functionality on sulcofuron, the effect of pH on extraction efficiency was investigated. This was performed by adjusting the pH of the spiked water samples. The analytes were eluted with methanol–ethyl acetate (1 + 1 v/v).

The doubly distilled, de-ionized water samples were spiked at the 1 μg l^{-1} (100 cm^3) matrix fortification level. The results (Table 3) illustrate that, like LLE, the SPE efficiency of sulcofuron is dependent on pH but with SPE the maximum efficiencies are obtained at pH 7. This is probably due to the suspected instability of the solid phase at low pH as the efficiencies of flucofuron and TCC are also affected. These analytes do not contain ionizable groups and so should largely be unaffected by pH changes in the matrix. This effect was revealed while performing LLE.

The solid-phase composition also affected the SPE efficiency dramatically. The specialty environmental phases gave no extraction efficiency for sulcofuron, which was not proven to be 100% breakthrough or 100% retention. The fact that the ENVI-CARB cartridge, based on a carbon black phase, did not extract any of the analytes is surprising because Di Corcia and Marchetti[13–15] described a rapid, sensitive method for 14 urons in aqueous samples using carbon black cartridges. The extraction efficiencies were reported to be 95–104 ± 4.6% (n = 6). The ENV+ cartridge, based on a styrene–divinylbenzene phase, extracted flucofuron and TCC with similar efficiencies to those of CH, C_8 and C_{18} phases, the three phases that gave the maximum recoveries for the three analytes.

The use of SPE was continued with the C_8 and C_{18} phases employing a variety of eluting solvents with differing polarities and desorption capabilities. The results (Table 4) reveal that the extraction efficiency is also dependent on the elution solvent. The maximum efficiencies (74.3 ± 8.4, 115.9 ± 3.1 and 112.7 ± 4.5% for sulcofuron, flucofuron and TCC, respectively) are obtained with a C_{18} cartridge using methanol as the eluting solvent. The effect of increasing the sample volume to 1000 cm^3 was investigated. No significant variation was observed, with extraction efficiencies of 76.3, 108.6 and 112.2% for sulcofuron, flucofuron and TCC, respectively.

The SPE recovery results are consistent with those obtained with the LLE method, but the precision of the SPE method (< 8.4%) is better than that obtained with the LLE method (< 14.3%).

Moore *et al.*,[9] Junker-Buchheit and Witzenbacher[11] and Patsias and Papadopoulou-Mourkidou[16] described rapid methods for determining urons in field water samples using a variety

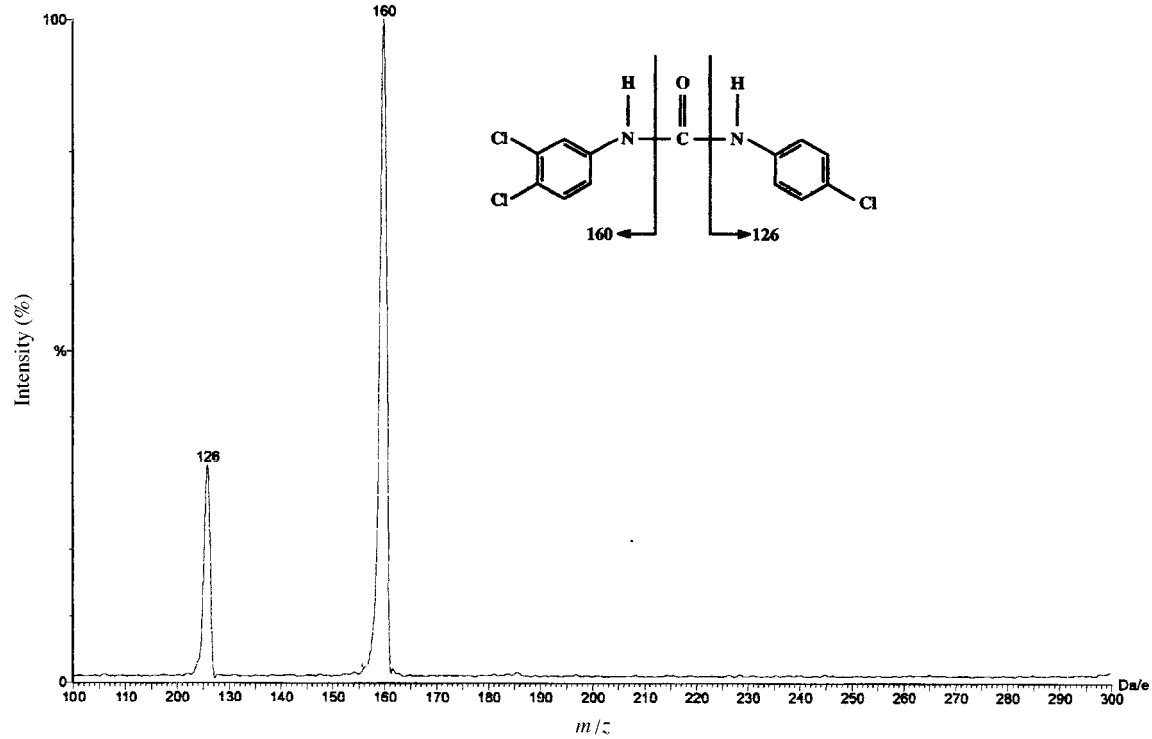

Fig. 5 TCC. Product-ion scan from *m/z* 313.

of solid phases. Moore *et al.*[9] reported extraction efficiencies for chlorotoluron, isoproturon, diuron and linuron of 101–118 ± 10% (n = 5). Junker-Buchheit and Witzenbacher[11] compared the extraction efficiency of a new polymeric sorbent and classical C_{18} cartridges for 10 urons. The extraction efficiency and precision with the C_{18} cartridge, 95–121 ± 4% (n = 6), was similar to those with the polymeric sorbent, 96–108 ± 4% (n = 3). Patsias and Papadopoulou-Mourkidou[16] reported extraction efficiencies for fluometuron, linuron, metobromuron and monolinuron of 78–95 ± 11% (n = 3). The mean recoveries and the extraction precision for sulcofuron, flucofuron and TCC are consistent with those reported for the selected urons.

Once again, environmental water samples were collected from the seven sites in the Meltham area of the River Calder catchment. Samples (1000 cm^3 aliquots) were extracted identically with the spiked samples. Analysis of the extracts by negative-ion LC–ESI-MS–MS operated in the MRM mode was performed.

The results for the environmental water samples are given in Table 1. Sulcofuron was detected in the highest concentrations at sites downstream of the sewage treatment works (HHB, 6.9 ng l^{-1}) and the textile mill (BR, 6.0 ng l^{-1}). Flucofuron was detected in the highest concentrations at sites downstream of the textile mill (BDII, 5.7 ng l^{-1}, and BDIII, 4.5 ng l^{-1}). These results are different from those obtained by employing LLE, but this is to be expected as there was an 18 month period between the sampling dates. The BDI and HR sites were used to confirm that the analytical method was not subject to interference as these sites are not known to have a history of contamination and were therefore expected to be clean.

The extraction efficiency of TCC was excellent for all the sites (93–110%) and illustrated that the method was reliable for the extraction of the analytes. The levels of sulcofuron and flucofuron monitored in environmental water were, again, well below the respective EQSs.

In conclusion LC–ESI-MS–MS operated in the MRM mode has continued to provide a highly sensitive and specific method of determination for sulcofuron and flucofuron in the environmental water matrix. LLE and SPE techniques with good reproducibility and efficiency have been successfully developed for the extraction of the analytes from environmental water. These extraction techniques, combined with the instrumental method of detection, allow the analytes to be determined at levels three to four orders of magnitude below their respective EQSs. The methods successfully employ an internal standard,TCC, to check extraction efficiency of the target analytes in quality control analysis. These methods have also been successfully applied to samples obtained from a contaminated ecosystem.

Table 3 SPE efficiencies for sulcofuron, flucofuron and TCC extracted from water using different extraction cartridges and pH values at 1 μg l^{-1}

		Recovery (%)		
Cartridge	pH	Sulcofuron	Flucofuron	TCC
CH	2	49.7	63.6	N.d.*
CH	7	74.0	129.1	83.1
C_8	2	47.3	124.6	N.d.
C_8	7	74.3	127.3	59.3
C_{18}	2	49.3	86.1	50.7
C_{18}	7	70.7	113.1	86.3
ENV+	2	N.d.	120.2	115.7
ENV+	7	N.d.	105.8	68.5
ENVI-CARB	2	N.d.	N.d.	N.d.
ENVI-CARB	7	N.d.	N.d.	N.d.

* N.d. = not detected (less than the LOD).

Table 4 SPE efficiencies for sulcofuron, flucofuron and TCC extracted from water using C_8 and C_{18} cartridges with different eluting solvents at 1 μg l^{-1} (n = 4)

		Recovery ± s (%)		
Cartridge	Elution solvent	Sulcofuron	Flucofuron	TCC
C_8	MeOH	72.7 ± 2.5	115.1 ± 6.8	112.6 ± 6.3
	MeOH–EtOAc	62.7 ± 10.4	76.4 ± 7.9	98.5 ± 7.4
	MeOH–acetone	61.8 ± 6.1	65.1 ± 5.1	88.7 ± 11.1
C_{18}	MeOH	74.3 ± 8.4	115.9 ± 3.1	112.7 ± 4.5
	MeOH–EtOAc	62.6 ± 5.7	80.1 ± 4.9	89.4 ± 5.6
	MeOH–acetone	62.3 ± 5.1	54.2 ± 5.8	93.3 ± 12.8

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