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# Monitoring of antifouling agents in water samples by on-line solid-phase extraction–liquid chromatography–atmospheric pressure chemical ionization mass spectrometry

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**Abstract**

An automatic method for determining diuron, irgarol 1051, folpet and dichlofluanid in seawater samples have been developed. This method is based on the on-line coupling of solid-phase extraction (SPE) with a highly crosslinked polymeric sorbent, LiChrolut EN, to liquid chromatography followed by atmospheric pressure chemical ionization (APCI) and mass spectrometry. The operational parameters affecting the APCI interface have been studied in both positive and negative ionization modes. The use of LiChrolut EN in the SPE produced recoveries of over 85% for all the compounds when 100 ml of seawater sample was preconcentrated. Calibration was carried out in both ionization modes and in full-scan and selected-ion monitoring (SIM). The method allowed all the analytes to be detected at 5 ng $l^{-1}$ in SIM acquisition mode except folpet, which, because of its low response, could only be detected at 250 ng $l^{-1}$. The method was used to analyse water samples taken from five different marina and fishing ports along the coast of Tarragona, Catalonia (Spain), over a 5-month period. Diuron and irgarol 1051 were detected and quantified in most samples at concentration levels ranging from 27 to 420 ng $l^{-1}$ for diuron and from 15 to 511 ng $l^{-1}$ for irgarol 1051. 

*Keywords:* Water analysis; Pesticides; Diuron; Irgarol 1051; Folpet; Dichlofluanid

## 1. Introduction

Antifouling compounds are used as additives in boat paints to prevent algae and other organisms from growing on the surface of the hull. Tributyltin (TBT) had been extensively used from the mid-1960s, but this compound and other organotin–copper-based antifouling agents were banned by the EU in 1989 from being used on boats under 25 m because of their effects on aquatic organisms [1]. As an alternative, new biocides like diuron and irgarol 1051 were introduced, but these are also toxic for marine algae, even at low concentrations [1–4]. Since some of them, such as irgarol 1051, have been found in seawater samples [1,5–7], there is a considerable interest in developing new analytical methods to determine simultaneously groups of antifouling agents and control their presence in seawater samples.

Gas chromatography (GC) using nitrogen–phosphorus detection (NPD) [8] or mass spectrometry detection (MS) [8–11] has been used to determine

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antifouling compounds in water samples. However, some compounds, like diuron, cannot be determined under these conditions because it degrades at high temperatures. For this reason, liquid chromatography (LC) has also been applied to the analysis of these types of pollutants, mainly with a diode-array detection (DAD) system [11], although in the last few years MS has been increasingly used because it can identify the analytes unambiguously [11–13]. Atmospheric pressure ionization techniques have become the most widely used interface for on-line coupling of LC and MS because it is highly sensitive and it is possible to obtain additional structural information by fragmenting the quasimolecular ion by applying sufficient voltage. This mode of operation is called preanalyser collision-induced deionization (CID).

Because these compounds are present in real samples at low concentration levels, a preconcentration step is necessary before chromatographic analysis. Liquid–liquid extraction (LLE) [8,10,11] and, recently, solid-phase microextraction (SPME) [14] have been used, but the most common enrichment technique is solid-phase extraction (SPE) because of its numerous advantages. Different kinds of sorbents, such as $C_{18}$ [5–8], graphitized carbon black, like Envi-carb [12], immunosorbents [15–17], or polymeric sorbents, like PLRP-s [5,9], have been used in the analysis of antifouling agents. Recoveries were generally good for all compounds, except the most polar ones, like dichlofluanid [9].

New highly crosslinked polymeric sorbents, such as LiChrolut EN and Isolute ENV+, have recently been developed. These sorbents have a higher degree of crosslinking than conventional polymeric sorbents and, therefore, a larger specific surface area which allows a greater retention of polar analytes [18,19].

The aim of this study was to develop an automatic method for determining four antifouling compounds in seawater samples: diuron, irgarol 1051, folpet and dichlofluanid. The method was based on the on-line coupling of SPE–LC–APCI–MS and the use of a highly crosslinked polymer, LiChrolut EN, as SPE sorbent. Finally, the method was used to monitor the presence of these compounds in seawater samples from five different ports along the coast of Tarragona, Catalonia, over a 5-month period.

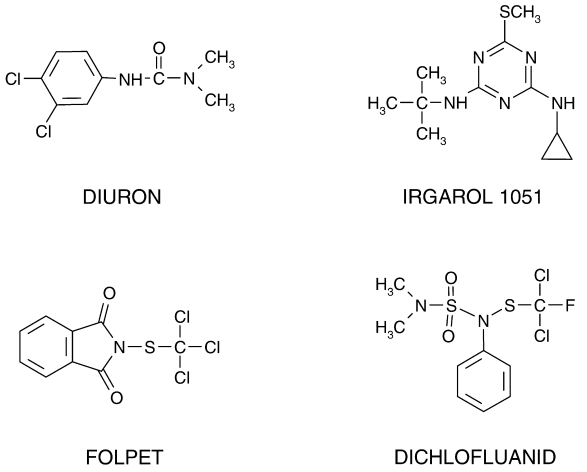


Fig. 1. Structures of the compounds.

## 2. Experimental

### 2.1. Reagents and standards

Fig. 1 shows the structure of the four antifouling agents used in this study. Three of these (diuron, folpet and dichlofluanid) were obtained from Riedel-de Häen (Seelze-Hannover, Germany) and had purities of over 98%, and one (irgarol 1051) was supplied by Ciba-Geigy (Barcelona, Spain), and had a purity of 100%. Stock standard solutions of each compound at a concentration of 2000 mg $l^{-1}$ were prepared in methanol HPLC grade (SDS, Peypen, France) and stored at 4°C. Working standard solutions of all the compounds were prepared by diluting the stock solutions in methanol and these were stored in the same way.

Acetonitrile HPLC grade (SDS, Peypen, France) was used as the organic component of the mobile phase. Acetic acid (Probus, Barcelona, Spain) was used to adjust mobile phase and sample pH. Ultrapure water was prepared by ultrafiltration with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

### 2.2. Instrumentation

An HP1100 series LC–MSD system (Agilent Technologies, Barcelona, Spain) with an APCI inter-

face was used for the analysis. This system allowed full-scan and SIM acquisition modes to be used simultaneously. The chromatographic system was equipped with an automatic injector, a degasser, a quaternary pump and a column oven. The chromatographic column was a 25.0×0.46 cm Kromasil 100 $C_{18}$ with a 5-μm particle size (Teknokroma, Barcelona, Spain).

SPE was carried out with a 10×3 mm stainless steel precolumn (Free University, Amsterdam, The Netherlands), laboratory-packed with 40–120 μm LiChrolut EN (Merck, Germany). This precolumn was on-line coupled to the chromatographic system by a Rheodyne 7010 valve, and an HP1100 isocratic pump was used to deliver samples and condition the precolumn.

### 2.3. Chromatographic separation

The mobile phase consisted of acetonitrile and water acidified to pH 3 with acetic acid. The gradient elution was as follows: the mobile phase started with 40% of acetonitrile, which was linearly increased to 55% in 12 min; then, over 12 min, the percentage was changed to 85% and returned to initial conditions in 4 min. The column was equilibrated for 5 min.

Column temperature was 65°C and the mobile phase flow-rate was 1 ml $min^{-1}$. For direct injection, the volume was 10 μl.

### 2.4. Mass spectrometry

The different operating parameters of the interface, including drying gas ($N_2$) flow, nebulizer gas pressure, vaporizer temperature, capillary voltage, corona current and fragmentor voltage, were optimized for each compound. Table 1 shows the optimum conditions for a mixture of all compounds for both positive and negative ionization modes.

Chromatograms were simultaneously recorded in full-scan ($m/z$=50–400) and under selected-ion monitoring (SIM) acquisitions. Irgarol 1051 was quantified in the positive mode by selecting ions 198 and 254. Folpet and dichlofluanid were quantified in the negative mode; in this case, the selected ions were 146 for folpet and 199 and 155 for dichlofluanid. We were able to quantify diuron in both positive and negative modes. In the positive mode, the selected ions were 233 and 72, and in the negative mode it was 231.

Table 1
Optimum conditions of the APCI interface for the simultaneous analysis of studied compounds

| APCI parameter | Ionization mode | |
|---|---|---|
| | Positive | Negative |
| Drying gas ($N_2$) (l $min^{-1}$) | 5 | 6 |
| Nebulizer gas pressure (p.s.i.) | 50 | 50 |
| Vaporizer temperature (°C) | 425 | 425 |
| Corona current (μA) | 5 | 7 |
| Capillary voltage (V) | 3000 | 3000 |
| Fragmentor (V) | 75 | 75 |

To improve sensitivity, quantification in full-scan mode was carried out by extracting the suitable peak from the obtained chromatogram.

### 2.5. Solid-phase extraction

All solvents and samples were percolated through the precolumn at a flow-rate of 4 ml $min^{-1}$. The precolumn was sequentially washed with 15 ml of methanol and 15 ml of water at pH 3, adjusted with acetic acid. The tubes were then purged with the sample solution, which had previously been acidified to pH 3 with acetic acid. A 100-ml volume of this sample was then preconcentrated and finally, the analytes were desorbed in the backflush mode by the mobile phase and on-line transferred into the chromatographic system.

### 2.6. Sampling

Seawater samples were collected at a depth of 1 m from the surface once a month between March and July 2000 from five different ports along the Mediterranean coast near Tarragona, Catalonia: the marina and the fishing ports of Tarragona and Cambrils and the port of Salou. As blank samples, seawater samples were also taken from the open sea.

All the samples were collected in 2.5-l precleaned amber glass bottles. They were filtered through a 0.45-μm membrane filter (Whatman, Maidstone,

UK), acidified to pH 3 with acetic acid and kept at 4°C in the dark until analysis.

## 3. Results and discussion

### *3.1. APCI–MS optimization*

The operational parameters of the APCI interface were optimized in both positive and negative ionization modes by the flow injection analysis (FIA) of a solution of each compound at a concentration of 50 mg $l^{-1}$ into a carrier stream of acetonitrile–acidified water (pH 3) (50:50). As optimum conditions, those in Table 1 were chosen. Under these conditions, folpet and dichlofluanid gave the highest abundance in the negative mode and irgarol 1051 gave the highest abundance in the positive mode. For diuron, results were similar in the two modes.

The fragmentor voltage, which is related to the molecule fragmentation, was studied for each compound in the 25–200 V range in both positive and negative ionization modes. Generally for low voltages, no fragmentation occurs and only the molecular ion is present in the corresponding spectra. However, at high voltages, fragmentation increases and there is a simultaneous decrease in sensitivity for the molecular ion, although more structural information is obtained. For example, Fig. 2 shows the abundance of the ions obtained for diuron in positive ionization mode as a function of the fragmentor voltage. We can see that the abundance of molecular ion ($m/z$ 233) decreases when the fragmentor voltage is increased whereas the abundance of the ion with $m/z$ 72, corresponding to the fragment $[MH-C_6H_5Cl_2N]^+$, increases. The other compounds behave in a similar way. Table 2 shows the most important fragment ions for each compound in its optimum ionization mode for two fragmentor voltages (75 and 125 V). No molecular fragment is obtained for folpet and dichlofluanid since fragmentation occurs even at low voltages.

### *3.2. Chromatographic separation*

The separation of the compounds was optimized by injecting a solution containing all the compounds at a concentration of 10 mg $l^{-1}$ directly into the chromatographic system. Finally, the gradient specified in Section 2.3 was selected. Under these conditions, separation lasted 21 min. The retention time for each compound is shown in Table 3.

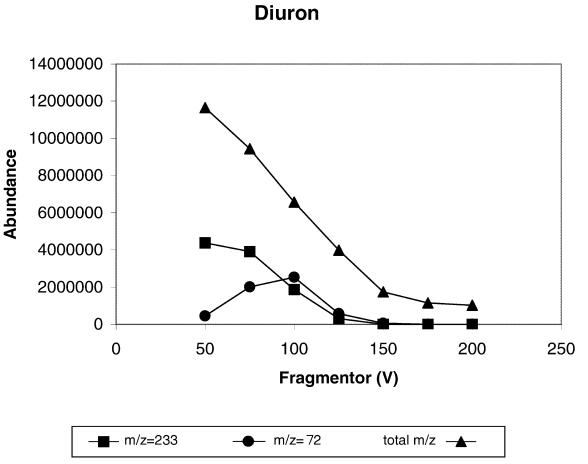


Fig. 2. Influence of the fragmentor voltage mode on the response in positive mode of a standard solution of diuron (50 mg $l^{-1}$) in a flow injection analysis using a carrier stream of acetonitrile–water (50:50).

Calibration models were constructed by injecting different standard solutions containing all the compounds at different concentration levels directly into the chromatographic system. The linearity was good for all the compounds between 0.1 and 100 mg $l^{-1}$ under the SIM acquisition mode, except for folpet, which could only be quantified in concentrations above 2.5 mg $l^{-1}$ because of its low response. The correlation coefficients were over 0.999. Calibration models were also constructed in full-scan acquisition mode. In this case, quantification was carried out by using the highest abundance peak for each compound. This was selected through the corresponding spectra to increase sensitivity but, as expected, quantification limits were higher (0.25–1 mg $l^{-1}$) than those under SIM acquisition. The correlation coefficients were over 0.994.

### *3.3. Optimization of SPE process*

As previously mentioned, LiChrolut EN was chosen as sorbent in the preconcentration step because of its high retention for polar analytes. To determine the recoveries and the breakthrough vol-

Table 2
Summary of the most important ions for each compound in its optimum ionization mode for two fragmentor voltages[a]

| Compound | $M_n$ | IM | 75 V | | 125 V | |
|---|---|---|---|---|---|---|
| | | | $m/z$ | R. A. (%) | $m/z$ | R. A. (%) |
| Diuron | 232 | P | 233 $[M+H]^+$ | 100 | 233 $[M+H]^+$ | 13 |
| | | | | | 72 $[MH-C_6H_5Cl_2N]^+$ | 100 |
| | | N | 231$[M-H]^-$ | 100 | 231 $[M-H]^-$ | 90 |
| | | | | | 186 $[MH-N(CH_3)_2]^-$ | 100 |
| Irgarol 1051 | 253 | P | 254 $[M+H]^+$ | 100 | 254 $[M+H]^+$ | 45 |
| | | | | | 198 $[MH-C_4H_7]^+$ | 100 |
| Folpet | 297 | N | 147 $[MH-SCCl_3]^-$ | 100 | 147 $[MH-SCCl_3]^-$ | 100 |
| Dichlofluanid | 332 | N | 199 $[MH-SCCl_2F]^-$ | 100 | 199 $[MH-SCCl_2F]^-$ | 25 |
| | | | 155 $[MH-SCCl_2FNCH_3]^-$ | 10 | 155 $[MH-SCCl_2FNCH_3]^-$ | 34 |
| | | | | | 91 $[MH-SCCl_2FSO_2N(CH_3)_2]^-$ | 100 |

[a] $M_n$, molecular mass; IM, ionization mode (P, positive; N, negative); R.A., relative abundance.

umes for the antifouling compounds, different volumes of Milli-Q water samples (10, 50, 100 and 200 ml) were percolated through the precolumn. These samples were spiked at different concentrations of the analytes, so that the amount of each analyte injected into the chromatographic system was kept constant (200 ng). The pH of these samples was adjusted to 3 with acetic acid. Table 3 shows the recoveries for each compound after preconcentration. For all the compounds, these were above 85%, even for dichlofluanid which could only be recovered at 67% in an on-line preconcentration of 10 ml of sample using PLRP-s as a sorbent [9] or at 20% in an off-line preconcentration of 500 ml of sample using LiChrolut EN cartridges [12].

Although a sample volume of 200 ml gave good recovery values, 100 ml was finally chosen because this was enough to achieve the concentration levels required for the analysis of these compounds in real samples and because analysis time was considerably longer for a higher sample volume.

Table 3
Retention time ($t_R$) and mean recoveries ($n=3$) for the on-line SPE–LC–APCI–MS analysis of spiked Milli-Q water samples with LiChrolut EN as a sorbent in the enrichment step

| Compound | $t_R$ (min) | Recovery (%)[a] | | | |
|---|---|---|---|---|---|
| | | 10 ml | 50 ml | 100 ml | 200 ml |
| Diuron | 10.1 | 97 | 97 | 98 | 99 |
| Irgarol 1051 | 15.7 | 95 | 93 | 92 | 91 |
| Folpet | 17.8 | 88 | 90 | 88 | 85 |
| Dichlofluanid | 20.3 | 89 | 89 | 89 | 87 |

[a] %RSD between 1 and 8% ($n=3$).

To study the capacity of the sorbent, the recoveries were checked for all compounds at different concentration levels. A 100-ml volume of seawater samples spiked with a concentration of between 0.05 and 100 μg $l^{-1}$ was preconcentrated. The recoveries were calculated and no significant differences were found.

### 3.4. On-line SPE–HPLC–APCI–MS calibration

Under optimum conditions, linearity was studied by preconcentrating 100 ml of seawater samples spiked with the antifouling compounds at a concentration of between 0.01 and 5 μg $l^{-1}$. The pH of the sample was adjusted to 3 with acetic acid. The calibration models were constructed using SIM and full-scan acquisition mode quantifying by extracting the highest abundance peak for each compound.

Table 4 shows the linear ranges, correlation coefficients and limits of detection for both SIM and full-scan acquisition modes. When SIM acquisition was used, models for diuron (negative ionization mode), irgarol 1051 and dichlofluanid were linear between 0.01 and 5 μg $l^{-1}$ and correlation coefficients were above 0.993. For diuron, calibration model under positive ionization mode was also possible, but in this case the quantification limit was 0.025 μg $l^{-1}$, although linearity was also good, with a correlation coefficient over 0.999. For folpet,

Table 4
Calibration results for spiked seawater samples in SIM and full-scan (quantification by extracting the specified peak) acquisition modes after preconcentration of 100 ml of the samples[a]

| Compound | | Ion ($m/z$) | Full-scan | | | SIM | | |
|---|---|---|---|---|---|---|---|---|
| | | | Linear range ($\mu g\ l^{-1}$) | $R^2$ | LOD ($\mu g\ l^{-1}$) | Linear range ($\mu g\ l^{-1}$) | $R^2$ | LOD ($\mu g\ l^{-1}$) |
| Diuron | PI | 72 | – | – | – | 0.025–5 | 0.9990 | 0.01 |
| | | 233 | 0.1–5 | 0.9998 | 0.05 | | | |
| | NI | 231 | 0.5–5 | 0.9998 | 0.2 | 0.01–5 | 0.9996 | 0.005 |
| Irgarol 1051 | PI | 198 | 0.1–5 | 0.9995 | 0.05 | 0.01–5 | 0.9995 | 0.005 |
| | | 254 | 0.025–5 | 0.9995 | 0.01 | | | |
| Folpet | NI | 146 | 1–5 | 0.9995 | 0.4 | 0.5–5 | 0.9991 | 0.2 |
| Dichlofluanid | NI | 155 | – | – | – | 0.01–5 | 0.9936 | 0.005 |
| | | 199 | 0.05–5 | 0.9988 | 0.02 | | | |

[a] PI, positive ionization mode; NI, negative ionization mode; $R^2$, correlation coefficient; LOD, limit of detection.

the quantification limit was higher (0.5 $\mu g\ l^{-1}$) due to its low abundance. These results are similar to those from the off-line preconcentration of 500 ml of sample using an LC–APCI–MS [12] and are slightly lower than those from SPE–GC–MS analysis [9], where 50 ng $l^{-1}$ was the quantification limit for irgarol 1051. For SPME–GC–MS, the quantification limit was higher (200 ng $l^{-1}$) [14].

The detection limits shown in Table 4, were calculated using a signal-to-noise ratio of 3.

Under full-scan acquisition mode, the compound abundances were studied in the same range of concentrations, and quantification limits were between 0.025 and 0.5 $\mu g\ l^{-1}$. Linearity was also good, with correlation coefficients above 0.998, and detection limits were between 10 and 100 ng $l^{-1}$. For folpet, these limits were 1 and 0.5 $\mu g\ l^{-1}$, respectively. Full-scan sensitivity was lower than in the SIM acquisition mode, but full-scan supplies some very useful information that could allow the analytes in real samples to be identified.

Repeatability and reproducibility between days of the method were evaluated by analysing five seawater samples spiked at a concentration of 0.1 $\mu g\ l^{-1}$ of diuron, irgarol 1051 and dichlofluanid and 1 $\mu g\ l^{-1}$ of folpet. Repeatability, expressed as relative standard deviation (RSD, %), was between 1 and 8%. As expected, reproducibility between days was higher, but this was acceptable taking into account the low levels of quantification. Expressed as RSD, results were between 12 and 18%, except

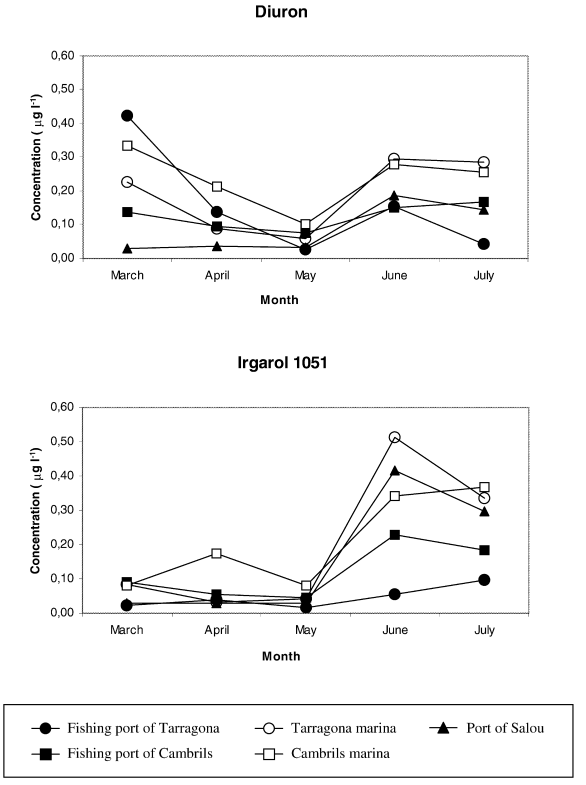


Fig. 3. Concentration of diuron and irgarol 1051 found in the samples from five different ports along the coast of Tarragona taken between March and July 2000.

with folpet, for which higher values were obtained due to its low response.

### 3.5. Application to real samples

The method was used to analyse seawater samples from five different ports along the coast of Tarragona (Catalonia, Spain) between March and July 2000.

Diuron and irgarol 1051 appeared in most of the samples. Fig. 3 shows the concentrations of diuron and irgarol 1051 obtained during this period. The highest levels of concentration correspond to periods when boats and yachts are painted or to the summer, when yachting activity is increased.

Diuron was found in all samples. In most of the ports, the highest concentration was generally found between March and July. Cambrils marina had the highest concentrations of diuron during the period (0.10–0.33 μg $l^{-1}$), but the most concentrated sample was taken in March from the fishing port of Tarragona.

Low levels of irgarol 1051 were generally found, although they increased considerably in most of the ports in June and July. The lowest concentration was found in the Tarragona fishing port (0.015–0.095

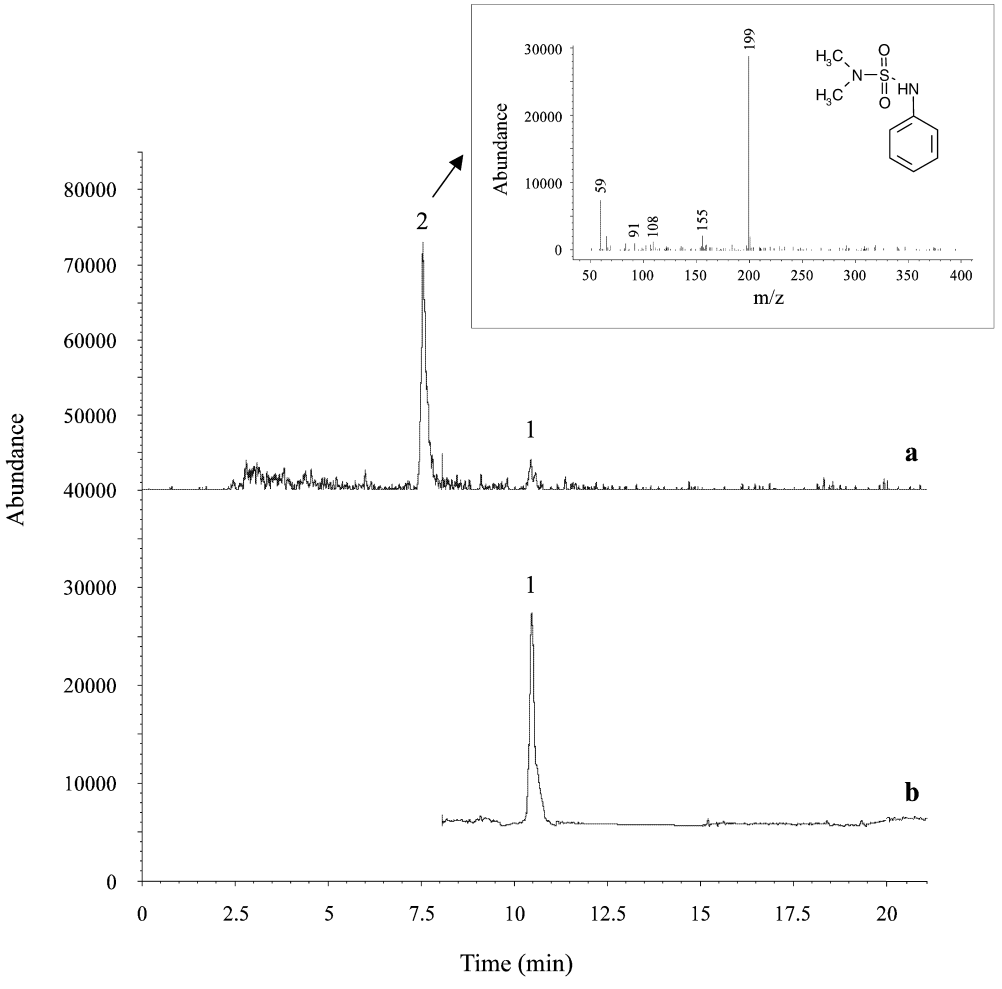


Fig. 4. Chromatograms obtained under full-scan (a) and SIM (b) acquisition in negative ionization mode for a Tarragona marina sample taken in June 2000. The concentration of diuron was 0.30 μg $l^{-1}$. Peaks: 1 = diuron; 2 = tentatively identified as N′,N′-dimethyl-*N*-phenylsulfonyldiamide. The MS spectrum of peak 2 and the structure of N′,N′-dimethyl-*N*-phenylsulfonyldiamide are also included.

μg $l^{-1}$) and the highest levels appeared in Cambrils marina (0.08–0.37 μg $l^{-1}$), although the most concentrated sample corresponded to one taken in June from the Tarragona marina.

The concentration levels are high when compared to those that were reported in the coast of Tarragona in 1999 [4], where diuron and irgarol 1051 were detected but could only be quantified in some samples presumably because the concentrations were below the determination level (0.05 μg $l^{-1}$). The highest concentrations of these compounds found corresponded to the Cambrils marina for diuron (0.6 μg $l^{-1}$) and the Salou port for irgarol 1051 (0.05 μg $l^{-1}$).

Figs. 4 and 5 show the chromatograms obtained in negative and positive ionization modes from a sample taken from the Tarragona marina in June 2000. In this sample, diuron and irgarol 1051 were found at concentrations of 0.30 and 0.51 μg $l^{-1}$, respectively.

Folpet was not found in these samples, nor was dichlofluanid, although a peak which appeared in some chromatograms obtained in negative ionization mode was tentatively identified as N′,N′-dimethyl-*N*-phenylsulfonyldiamide, which has been reported to be a degradation product of this compound [20]. The obtained spectrum and the structure of this compound is shown in Fig. 4, which Akiyama et al. [20] determined using a GC–MS system. For this reason, their spectra cannot be compared to ours, but some peaks do coincide. Moreover, all the majority peaks could be tentatively identified: these were 199, 155, 108, 91 and 65, which corresponded to the fragments $[C_6H_5NHSO_2N(CH_3)_2-H]^-$,

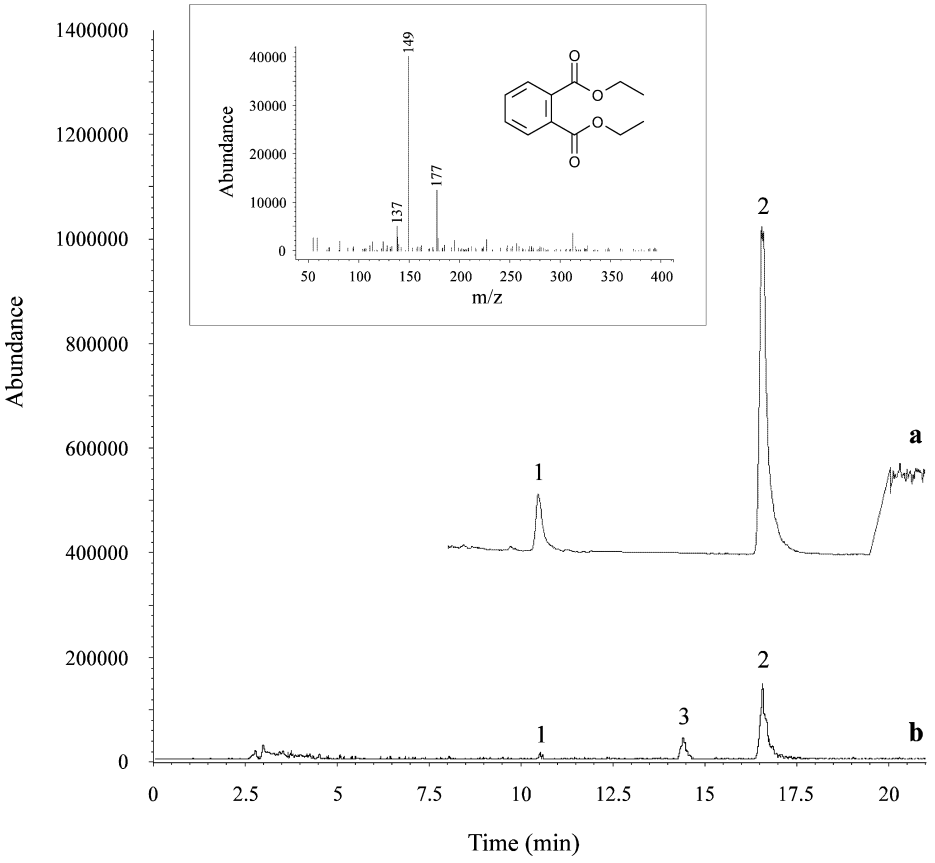


Fig. 5. Chromatograms obtained under SIM (a) and full-scan (b) acquisition in positive ionization mode for a Tarragona marina sample taken in June 2000. The concentrations of diuron and irgarol 1051 were 0.30 and 0.51 μg $l^{-1}$, respectively. Peaks: 1=diuron; 2=irgarol 1051; 3=tentatively identified as diethylphthalate. The MS spectrum of peak 3 and the structure of diethylphthalate are also included.

$[C_6H_5NHSO_2]^-$, $[C_6H_5NH]^-$, $[SO_2N(CH_3)_2]^-$ and $[SO_2]^-$, respectively. They could not be identified by retention time because the standard of this degradation product was not available.

Another peak was tentatively identified as a phthalate because it presented ions 149 and 177, as can be seen in Fig. 5, where the spectrum is shown. The first is a typical fragment that appears in the spectrum of this type of compound and corresponds to $[C_6H_4COOCO+H]^+$ [21]. The second is typical of diethylphthalate and corresponds to $[C_6H_4COOCOCH_2CH_2]^+$. A standard of this compound was available, so it was directly injected into the chromatographic system and the spectrum and the retention time were similar.

## 4. Conclusions

An automatic method based on the on-line coupling of SPE–LC–APCI–MS has been developed to determine four antifouling compounds in seawater samples. The highly crosslinked polymer LiChrolut EN, used as sorbent in the SPE step, allowed all the compounds, even the most polar ones such as dichlofluanid, to be recovered at more than 85% when 100 ml of sample was preconcentrated. These recovery values and the high sensitivity of the MS detection under SIM acquisition mode with an APCI interface allowed the quantification of all the compounds at low concentration levels (10 ng $l^{-1}$), except folpet which could only be quantified at 500 ng $l^{-1}$ because of its low response. Repeatability and reproducibility of the method between days were also evaluated and good results were obtained. This automatic method allowed monitoring of the presence of some of the compounds in samples taken from different ports along the coast near Tarragona. Only diuron and irgarol 1051 could be detected and quantified at concentration levels of 27–420 and 15–511 ng $l^{-1}$, respectively.

Moreover, some additional peaks were tentatively identified as diethylphthalate and a degradation product of dichlofluanid.

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