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Ultra-trace-level determination of the antifouling agent Irgarol 1051 by gas chromatography with tandem mass spectrometric detection

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Abstract

The contamination level of the *s*-triazine herbicide Irgarol 1051, which is used as the active ingredient in antifouling paints, was studied in the Western Scheldt estuary. The combined use of large-volume injection gas chromatography and ion trap (MS–MS) detection, enabled identification and quantification at the 0.1–1 ng/l level. By using tandem mass spectrometric detection (MS–MS), rather than conventional MS, a great gain in selectivity was achieved. The concentration levels found ranged between 1 and 10 ng/l.

Keywords: Programmed-temperature vaporizer; Environmental analysis; Water analysis; Irgarol 1051; Pesticides; Triazines

1. Introduction

In the late 1980s, several countries restricted the use of tri-*n*-butyltin (TBT) as an active ingredient in antifouling paints for small boats because of severe damage to non-target populations, such as bivalves and gastropods in the sea. Since then, new formulations have been introduced and copper compounds have largely replaced TBT as the active agent, often in combination with algicides such as Irgarol 1051 [1].

The herbicide Irgarol 1051 [2-methylthio-4-*tert.*-butylamino-6-cyclopropylamino-*s*-triazine] is an *s*-triazine (for its structure, see Fig. 1) that is manufactured by Ciba-Geigy in Switzerland and the USA. Apart from a minor application in the preparation of paints used, for example, on concrete roofing tiles [1], its major application is in antifouling paints. Irgarol 1051 has a solubility in water of 7 mg/l and a log K_{ow} of 3.6. To date, only a few studies have been published on the presence of Irgarol 1051 in environmental samples [2–5]. An overview of the results is presented in Table 1. Not surprisingly, the concentrations of Irgarol 1051 in water from marinas are much higher, i.e., often typically 100–700 ng/l, than those in coastal and estuarine waters, which mostly are in the 1–40 ng/l range.

A study has been reported on the toxic effects of Irgarol 1051 on periphyton communities in coastal water microcosms [2]. It was shown that Irgarol

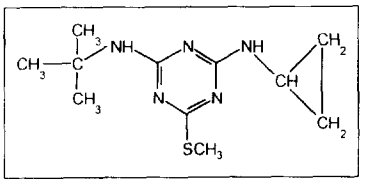

Fig. 1. Structure of Irgarol 1051.

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Table 1
Concentrations of Irgarol 1051 in a marine environment

Location	Date	Concentrations of Irgarol 1051 (ng/l)				Reference
		Marinas	Ports	Estuarine	Coastal areas	
West coast Sweden	May–Sept. 1994	30–400	n.s.	n.s.	n.d.	[2]
Côte d'Azur, France	June 1992	110–1700	<5–280	n.s.	n.d.	[3]
Southern England	July–Sept. 1993	52–500	9–14	4–18	<2–11	[4]
Eastern England	April 1995	682	n.s.	1–39	n.s.	[5]
Eastern England	June 1995	536	n.s.	<1–10	n.s.	[5]
Eastern England	Sept. 1995	169	n.s.	4–10	n.s.	[5]

n.s.: not sampled; n.d.: not detected.

1051 is highly toxic to non-target marine algae and that it is sufficiently persistent and mobile to reach toxic concentrations in certain areas in the marine environment. It was concluded that the fate and effects of Irgarol 1051 require substantial further evaluation, and that combined effects due to the presence of other herbicides that have similar structures and modes of action should also be considered [2]. In view of the environmental concern about Irgarol 1051 and the lack of environmental data, we decided to try to detect Irgarol 1051 in the river Scheldt and its estuary, the Western Scheldt (Netherlands), which is a dense shipping lane, i.e., for Antwerp (Belgium), Terneuzen and Vlissingen (Netherlands), and also to improve the analytical procedure by using gas chromatography with tandem mass spectrometric detection (GC–MS–MS) rather than with conventional MS or thermionic detection. The latter aspect should help to reduce the volume of water sample required per analysis.

2. Experimental

2.1. Materials

Irgarol 1051 was obtained from Ciba-Geigy (Basle, Switzerland). Stock solutions of 1 mg/g were prepared in freshly distilled reagent-grade ethyl acetate from J.T. Baker (Deventer, Netherlands) and stored in the dark at −20°C.

2.2. Samples

Water samples were taken from the Scheldt and Western Scheldt at different sites along the salinity gradient in April 1996. Samples were taken at a depth of 1 m by a pumping system that was equipped with a salinity monitor. Extraction of a 200-ml sample was performed on board the sampling vessel by solid-phase extraction (SPE) by means of Empore styrene–divenylbenzene (SDB) extraction disks (47 mm in diameter) obtained from J.T. Baker. The main advantages of extraction disks over standard SPE cartridges are the high sampling flow-rates and a fast mass transfer. The disks were conditioned with 10 ml of pesticide-grade acetone, obtained from Promochem (Wesel, Germany), followed by 10 ml of HPLC grade methanol from J.T. Baker. After drying the disk, a 0.45-μm hydrophilic Durapore filter (Millipore, Etten-Leur, Netherlands) was placed on top of the extraction disk. Its selection was based on its compatibility with the solvent used for conditioning the disk. Both were conditioned with another 10 ml of methanol and rinsed with 20 ml of HPLC-grade water (J.T. Baker), followed by the sample without allowing the disk to run dry in between. Next, a 200-ml sample was passed through the filter at a flow-rate of 10 ml/min. After drying the disks for at least 30 min, they were stored in the dark at −20°C. Elution of the disks was performed in the laboratory with 3×5 ml of ethyl acetate. After addition of an internal standard (PCB 103), the extracts were evaporated to 200 μl under a stream of nitrogen.

2.3. Analysis

A 40-μl sample of the 200 μl final extract was injected at an injection speed of 1.7 μl/s with a Model 8200 autosampler (Varian, Walnut Creek, CA, USA) into a Gerstel (Mülheim, Germany) C1S 3

programmable temperature vaporizer (PTV). An empty liner with swirled holes and an internal diameter of 1.2 mm was used. Evaporation of the solvent occurred at a split flow-rate of 170 ml/min, with a purge time of 38 s. The injector was programmed from 40°C (38 s) at 8°C/s to 280°C (10 min), with a splitless time of 2 min. A Varian GC coupled with a Varian Saturn III ion trap detector (ITD) was used with a DB5-MS column of 30 m×0.25 mm I.D. and a film thickness of 0.25 μm (J & W, Folsom, CA, USA). A retention gap of 2 m×0.53 mm I.D. deactivated fused-silica (Chrompack, Middelburg, Netherlands) was used as the guard column. Helium was used as the carrier gas (35 cm/s). The GC temperature programme was from 60°C (2 min) at 10°C/min to 300°C (15 min). Electron impact (EI) ionization and positive chemical ionization (PCI) were used with HPLC-grade acetonitrile (J.T. Baker) as the reagent gas. The following standard settings were used: Transfer line temperature, 285°C; manifold temperature, 230°C; A/M amplitude voltage, 4.0 V; scan rate, 200 ms; mass scan range, 50–450 *m/z*; non-resonant excitation; isolation window, 3 *m/z*; excitation time, 20 ms; low digital-to-analog converter (DAC) offset, six DACs; high DAC offset, two DACs; isolation time, 5 ms; ejection storage level, 48 *m/z*; ejection amplitude, 20 V; broadband amplitude, 30 V; target value 5000. PCI experiments were performed in the 'selected ejection' mode. The settings for this mode were: ARC ionization time, 1000 μs; CI maximum ionization time, 1000 μs; CI maximum reaction time, 30 ms; CI ionization storage level, *m/z* 20; reagent ion ejection amplitude, 7.5 V; CI reaction storage level, *m/z* 20; CI background mass, 60 *m/z*.

3. Results and discussion

Even with sophisticated analytical techniques such as GC–EI–MS, the low ng/l detection of organic microcontaminants in complex water samples often requires the processing of several litres of water. Sampling becomes especially tedious and time-consuming with estuarine water samples with high contents of suspended matter, such as those used in the present study, where the low-salinity samples often caused blocking of the filter (see Section 2) with volumes over ca. 250 ml. To make up for the loss of analyte detectability caused by the use of a 200-ml sample volume only, we used large-volume injection GC. That is, 40 μl injections were made, rather than the conventional 1–2 μl injections. In order to improve the system's performance still further, ion-trap MS–MS detection with its inherently high selectivity was compared with the usual MS-type of detection. Generally speaking, the use of MS–MS in the non-resonant mode requires the optimization of two parameters, i.e., the excitation radio frequency (RF) storage level and the excitation voltage applied during the collision-induced dissociation (CID) step. The RF storage level was set to 75 *m/z* to allow both efficient isolation of the parent ion and efficient trapping of product ions. The CID excitation voltage was optimized with the aid of the automated method development (AMD) software. The molecular ion *m/z* 253 was selected as the parent ion and an optimum CID excitation voltage of 50 V was found after only three injections of a standard solution. The recovery of the SPE procedure for Irgarol 1051 was studied by spiking a river Scheldt water sample ($n=5$) at the 0.1 μg/l level. After correction for the natural concentration of Irgarol 1051 in the sample (6.5±0.8 ng/l; $n=3$), a recovery of 101%, with a relative standard deviation of 8.7%, was found. The repeatability of the PTV large-volume injection for Irgarol 1051 was 5.3% (2.5 μg/l standard solution; $n=9$) and calibration plots were linear ($r^2=0.995$; nine data points) in the range tested (10 and 3000 pg of injected compound, which corresponds to a range of 0.25–75 ng/l in the sample).

As an example, Fig. 2 shows GC–EI–MS (Fig. 2a) and GC–EI–MS–MS (Fig. 2b) chromatograms for a river Scheldt water sample. The inserts at the top show spectra obtained for a standard solution of Irgarol 1051 in ethyl acetate (1 ng injected); the lower inserts are the non-background subtracted spectra for the sample at the retention time expected for Irgarol 1051. Our EI–MS spectrum for the Irgarol 1051 standard was essentially the same as that published by Gough et al. [4], with *m/z* 182 (ion $[M-NC(CH_3)_3]^+$) being the base peak and other major ions at *m/z* 253, 238 and 196. The spectrum published by Readman et al. [3] is somewhat different, with *m/z* 253, the M^+ ion, being the base peak

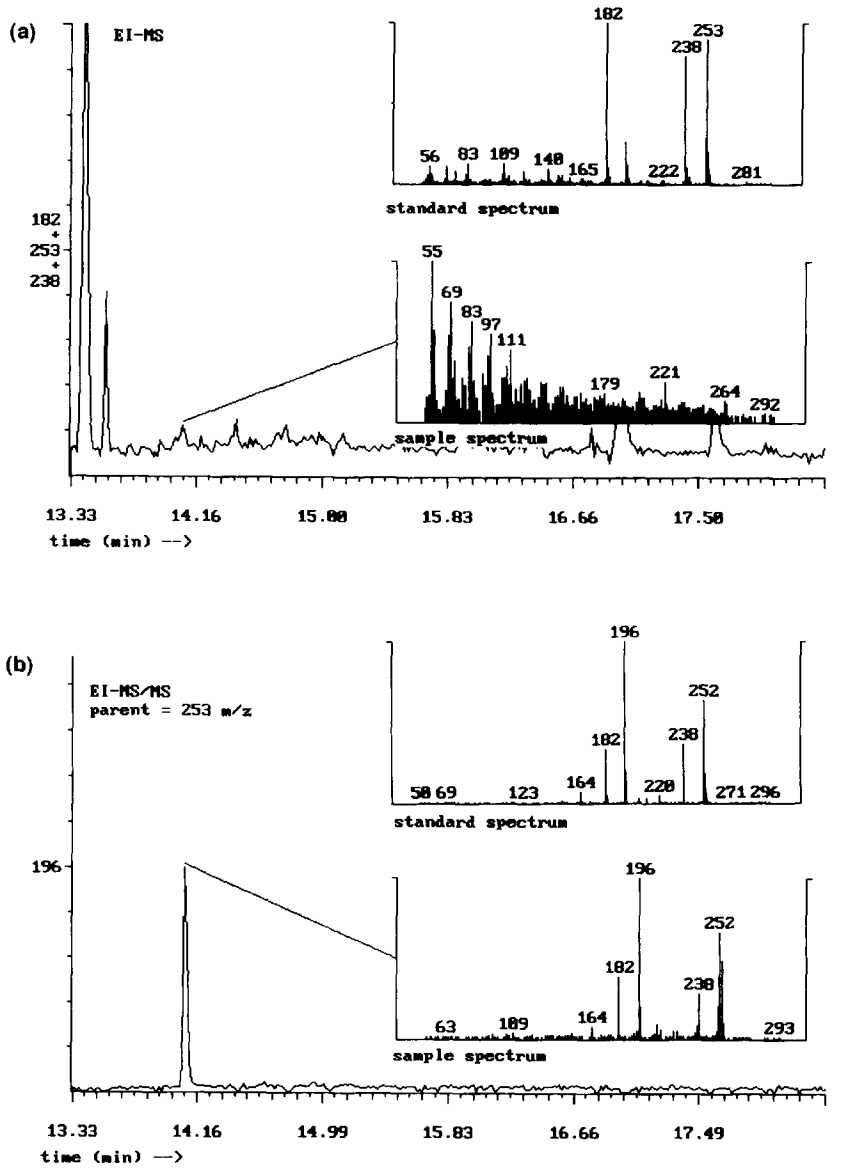

Fig. 2. (a) GC–EI–MS chromatogram (m/z 182+238+253) obtained after the analysis of a river Scheldt water extract. Top inset, spectrum that was obtained for an Irgarol 1051 standard solution in ethyl acetate (1 ng injected). Bottom inset, spectrum recorded at the expected retention time. (b) GC–EI–MS–MS product chromatogram (m/z 196) obtained after analysis of the same sample. Spectra of standard (top) and sample peak (bottom) are compared. For all other experimental details, see text.

and m/z 182 at an abundance of 40%. It should be stated that the latter spectrum was obtained for a coastal water extract, whereas the former two were obtained for standard solutions. For the lower inset of Fig. 2a, it is obvious that the presence of Irgarol 1051 in the river water extract cannot be confirmed unambiguously by means of GC with EI–MS detection because of the high background level. This background is almost eliminated when using EI–MS–MS, as is demonstrated by comparing the

inserts of Fig. 2b. Quantification was performed with the product ion m/z 196; the prominent peak in Fig. 2b represents a level of (6.5±0.8) ng/l. In EI–MS–MS, the limit of determination (S/N ratio=20) was found to be 1 ng/l for the surface water sample, and the limit of detection (S/N ratio=3) was 0.1 ng/l.

The presence of Irgarol 1051 in the river Scheldt sample was further confirmed with PCI–MS–MS. Using acetonitrile as the reagent gas, the predominant peak in the PCI–MS spectrum was the protonated molecular ion, $[M+H]^+$ m/z 254 (there were no major fragment ions). This ion was selected as the parent ion in CI–MS–MS. The RF storage level was set to 75 m/z and an optimum CID excitation voltage of 50 V was found. A product ion with m/z 198 was formed, together with ions of m/z 164, 182 and 238, which were also present in the EI–MS–MS spectrum. These ions had an abundance of approximately 10% of the major product ion. The quality of the data obtained in GC–PCI–MS–MS was such that confirmation of the presence of the antifouling agent was possible down to at least 1 ng/l.

3.1. Application

As an application, we investigated the profile of Irgarol 1051 along the salinity gradient in the Western Scheldt. The results are shown in Fig. 3.

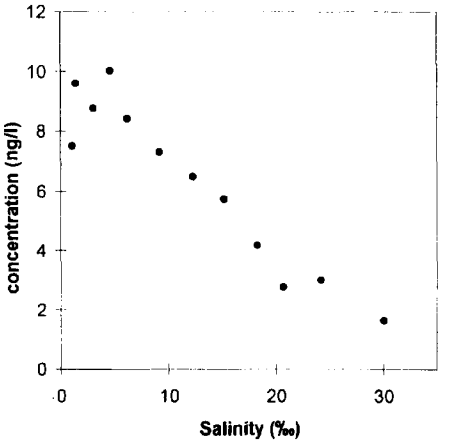

Fig. 3. Salinity–concentration profile for Irgarol 1051 in the Western Scheldt. Samples were taken in April 1996.

The concentration of Irgarol 1051 decreased from a level of about 8–10 ng/l at low salinity (1–4‰), corresponding to locations slightly upstream of Antwerp to approximately 2 ng/l at high salinity (25–30‰), encountered at locations in the mouth of the estuary. The apparent linear relationship between the concentration of Irgarol 1051 and the salinity was somewhat surprising, as it may point to a riverine input followed by conservative behaviour of Irgarol 1051 in the estuary (i.e., dilution caused by mixing of contaminated fresh water with seawater). The main source of Irgarol 1051 was expected to be the shipping traffic, in which case the relationship between Irgarol 1051 and salinity does not have to be linear. More detailed investigations are required, however, in order to obtain more insight into the sources of Irgarol 1051. The concentration levels found are in line with data reported in literature for estuaries and coastal zones (see Table 1).

4. Conclusions

The combined use of large-volume (40 μl) injection GC and ion trap (MS–MS) detection enabled the identification and quantification of the antifouling Irgarol 1051 at the 0.1–1 ng/l level. A sample volume of 200 ml suffices to reach this goal, which is highly advantageous because it permits the rapid and instantaneous filtration and extraction of even low-salinity estuarine samples, without blocking the filter due to the high level of suspended matter present. The use of EI–MS–MS rather than EI–MS detection gives rise to a great gain in selectivity. PCI–MS–MS was successfully used for analyte confirmation. The ruggedness and user-friendliness of the GC–ion trap (MS–MS) system has encouraged us to further implement the present approach for the improved detection of a wide range of (target and unknown) microcontaminants.

The target analyte of the present study, Irgarol 1051, was detected along the salinity gradient in the Western Scheldt estuary. Concentration levels between 1 and 10 ng/l were found. These levels are similar to concentrations reported for estuaries in Southern and Eastern England. The data may point to a riverine input and conservative behaviour of

Irgarol 1051 in the estuary but more research is needed to confirm this interpretation.

Acknowledgments

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