Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1046 (2004) 41–48
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Microwave-assisted extraction of Irgarol 1051 and its main degradation product from marine sediments using water as the extractant followed by gas chromatography–mass spectrometry determination

Georgia Gatidou[a,b], John L. Zhou[a], Nikolaos S. Thomaidis[c,*]

[a] *Department of Biology and Environmental Science, School of Life Sciences, University of Sussex, Falmer, Brighton BN19QJ, UK*
[b] *Laboratory of Water and Air Quality, Department of Environmental Studies, University of the Aegean, University Hill, 81100 Mytilene, Greece*
[c] *Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimioupolis Zografou, 15771 Athens, Greece*

Received 27 February 2004; received in revised form 28 May 2004; accepted 23 June 2004

Abstract

A microwave-assisted extraction (MAE) method for the determination of Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-s-triazine) and its main degradation product M1 (2-methylthio-4-tert-butylamino-s-triazine) in marine sediments by gas chromatography–mass spectrometry (GC–MS) was developed. The key parameters of MAE procedure, including the amount of the sediment, the volume of the extraction solvent, the duration and the temperature of the extraction procedure were optimized. The extraction procedure was followed by solid-phase extraction (SPE) on reverse phase C_{18} cartridges. The isolation of the target compounds from the matrix was found to be efficient when 3 g of marine sediment were extracted with 30 ml of water for 10 min at 115 °C. Final determination was accomplished by GC–MS. Quantification was performed with matrix-matched calibration using atrazine-d_5 as internal standard. Mean recoveries higher than 85.4% were obtained for both compounds at three fortification levels with relative standard deviations (R.S.D.) ≤ 14%. The limits of detection (LOD) of the developed method were 0.9 and 1.7 ng g^{-1} dry weight for M1 and Irgarol 1051, respectively.

Keywords: Microwave-assisted extraction; Marine sediment; Irgarol 1051

1. Introduction

The search for new sample extraction methods in environmental analysis which are simple, rapid and efficient has always been a challenge. Recently, as an alternative to conventional extraction methods, microwave-assisted extraction (MAE) has been developed. This technique is based on the absorption of the microwave energy by extraction solvents resulting in an increase of the temperature and pressure, thus, diffusion of the compounds from the matrix to the solvent can be achieved [1].

Compared with traditional extraction methods such as ultrasonication, MAE has many advantages: smaller volumes of solvents are needed, the extraction time is shorter due to the direct heating of the solvents by microwaves and multiple samples (up to 14) can be extracted simultaneously [2]. Moreover, the presence of water in the samples can be a significant benefit in MAE procedures [3]. Water improves the recoveries of the target compounds [3–5], helps non-polar organic solvents to absorb the microwave energy [6], and by itself can be used for the extraction of some organic compounds [3,7–10]. However, the MAE has some drawbacks as well. The extraction solvent must be able to absorb the microwave energy. A clean-up step is needed due to co-extraction of matrix material in the sample, which can cause interferences in chromatographic separations [2,7].

* Corresponding author. Fax: +30 210 7274750.
E-mail address: ntho@chem.uoa.gr (N.S. Thomaidis).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.06.071

Moreover, if water is used as extractant, transfer of analytes into an organic solvent should be performed before GC/MS analysis.

The triazinic compound Irgarol 1051, which is used in antifouling paints as booster biocide often in combination with copper, and its main degradation product after biodegradation, photodegradation and chemical hydrolysis [11–13] have been extracted from sediment samples using several procedures. Soxhlet extraction [14], supercritical fluid extraction [15,16], mechanical agitation [17,18], sonication [19–23], or both mechanical agitation and sonication have been used [24–26]. However, up to now, no MAE procedure has been developed for the extraction of these compounds from marine sediments.

Thus, the objective of this work was the development and optimization of a MAE method for the simultaneous determination of Irgarol 1051 and its main degradation product, M1, from marine sediments by GC–MS. For this purpose, water was used as the extraction solvent instead of the widely used organic solvents. The key parameters in MAE, including the amount of the extracted sediment, the volume of water and the duration and temperature of the extraction procedure were carefully studied. Furthermore, the method developed was applied to natural samples from the marine environment for the determination of Irgarol and M1.

2. Experimental

2.1. Sampling

For the spiking experiments, surface sediment samples were collected from Seven Sisters, which is located 16 miles to the east of the city of Brighton & Hove (UK), with a hand held Van Veen sediment grab. Using a stainless steel spoon, the samples were transferred to solvent rinsed jars and stored in the dark at −18 °C. Prior to spiking experiments, the samples were analyzed to ensure that they were free of the analytes.

Following successful development, the method was applied for the determination of Irgarol and M1 from natural sediment samples from Shoreham Harbour, southern England. Sampling was performed in May 2003, after which samples were kept at −18 °C until analysis.

2.2. Chemicals

Analytical standard of Irgarol 1051 was supplied by Dr. Ehrenstorfer (Germany). M1 was a gift of both Center for Environment, Fisheries and Aquaculture Science (Essex, UK) and Ciba-Geigy (NY, USA). Deuterated atrazine (atrazine-d_5) was purchased from QMX Laboratories (UK) and used as internal standard. Silica-based bonded C_{18} cartridges (Isolute, 1 g) were supplied by International Sorbent Technologies (UK). The organic solvents acetonitrile, dichloromethane, methanol and acetone were of glass distilled grade (Rathburns, Scotland). Ultrapure water was prepared in the laboratory with a Maxima HPLC/LS system supplied by ELGA (UK). Stock solutions of Irgarol 1051 and M1 were prepared in methanol at 1000 mg l^{-1} whereas for atrazine-d_5, a stock solution at 500 mg l^{-1} was prepared. The stock solutions were kept at −18 °C, from which working standard solutions were regularly prepared.

2.3. Choice of the best parameters for the MAE procedure

In order to maximize the potential of MAE, various key parameters, which may affect the efficiency of extraction, were studied in detail. The first parameter, which was checked for the optimization of MAE, was the mass of the sediment. Initially, the marine sediment was homogenized and weighed (1, 2, 3, 5 and 10 g dry weight, respectively) directly into the PTFE lined vessels. The internal standard and the target compounds (100 ng each) were used for spiking the sediment, to which acetone (2 ml) was added in order to form a slurry. The vessels were left in a fume cupboard overnight to remove the organic solvent, after which, ultrapure water (30 ml) was added and the vessels symmetrically placed on the microwave turntable. The extraction was carried out at 105 °C for 3 min, after which, the vessels were cooled to room temperature and the supernatant decanted. The sediment was then rinsed three times with 10 ml of ultrapure water and the supernatants were combined. These were centrifuged for 5 min at 2500 rpm to separate supernatant from sediment fine particles, with the supernatant being collected and directly extracted by SPE.

The SPE procedure used in this study was developed and described in detail in a previous work [23]. Briefly, C_{18} cartridges were activated with 10 ml of methanol plus 10 ml of ultrapure water. The extraction was performed at a flow rate of 10 ml min^{-1}. Then, the cartridges were washed with 4 × 2.5 ml of ultrapure water, dried for 3 min and eluted with 3 × 2 ml of methanol. The eluents were evaporated until dryness under a gentle stream of nitrogen (35 °C) and the compounds were dissolved in 300 μl of ethyl acetate. The recoveries of the SPE procedure were quantitative for both the compounds, as described previously [23].

The above procedure was followed so as to determine the optimum values of the extraction solvent (10, 15, 25 and 40 ml of water), the duration of the microwave extraction (5, 10, 15 and 20 min) and the temperature of the microwave extraction (100, 115, 120 and 130 °C). Eventually, from all the extraction experiments the optimum value for each parameter was chosen and the optimized method was applied to spiked sediments in order to confirm that the selection of the values was appropriate. Significant differences between the recoveries from the optimization experiments were tested using the least significant difference multiple range test (L.S.D. test) using the appropriate statistical software (SPSS for Windows, Version 11.0, SPSS Inc., 2001).

2.4. MAE apparatus

The microwave extraction of the target compounds was performed using a MARS-X laboratory microwave accelerated extraction system, with a maximum power of 1200 W, operated in the close mode (CEM, Matthews, NC, USA). The instrument is configured with a 14-position carousel and the extraction can either be temperature- or pressure-controlled. During extraction, the temperature and the pressure are monitored in a single vessel (control vessel) by a sensor, while another sensor monitors any solvent leaks in the interior of the microwave oven. In the present study, the selected control type was "ramp to temperature" while the pressure was constant at 200 psi. The magnetron power was 100% (600 or 1200 W, depending on the number of samples simultaneously extracted). The time to reach the settings was set to 7 min.

2.5. GC–MS analysis

For the quantitative analysis a Trace GC 2000 connected to a Polaris Q ion trap mass spectrometer was used (ThermoQuest CE Instruments, Texas, USA) supported by an autosampler (AS 2000). The separation of the compounds was achieved by using a ZB-5 (5% diphenyl–95% dimethylpolysiloxane) capillary column (30 m) with a film thickness of 0.25 μm and internal diameter of 0.25 mm (Phenomenex, UK). The carrier gas was helium and maintained at a constant flow rate of 1 ml min^{-1}. A sample volume of 1 μl was injected in splitless mode at an inlet temperature of 220 °C. The column temperature was programmed from 70 to 175 °C at 20 °C min^{-1}, from 175 to 185 °C at 2 °C min^{-1}, from 185 to 300 °C at 10 °C min^{-1} and maintained at this temperature for 2 min. The MS transfer line temperatures was maintained at 280 °C, whereas the ion source temperature was 220 °C. Electron impact (EI) mass spectra were obtained at 70 eV ionization energy.

For the qualitative analysis, the full scan mode was used, monitoring the mass range from 50 to 650. Quantitative analysis was carried out using selected ion monitoring (SIM) mode. For each compound, the three most abundant ions were selected from its spectrum. The chosen ions were 205 (100), 178 (41) and 220 (38) for atrazine-d_5, 157 (100), 198 (77) and 213 (32) for M1 and 182 (100), 253 (61) and 238 (56) for Irgarol 1051. The values in parentheses give the relative abundance (%). Our EI–MS spectrum for Irgarol 1051 was essentially the same as that reported previously [14,19,25]. A typical chromatogram of the target compounds and their mass spectrum in SIM mode are shown in Fig. 1.

2.6. Validation of the method

The instrument calibration was carried out using eight different concentrations (0.02, 0.05, 0.10, 0.30, 0.50, 0.80, 1.0 and 2.5 mg l^{-1}) of each compound, with three replicates per

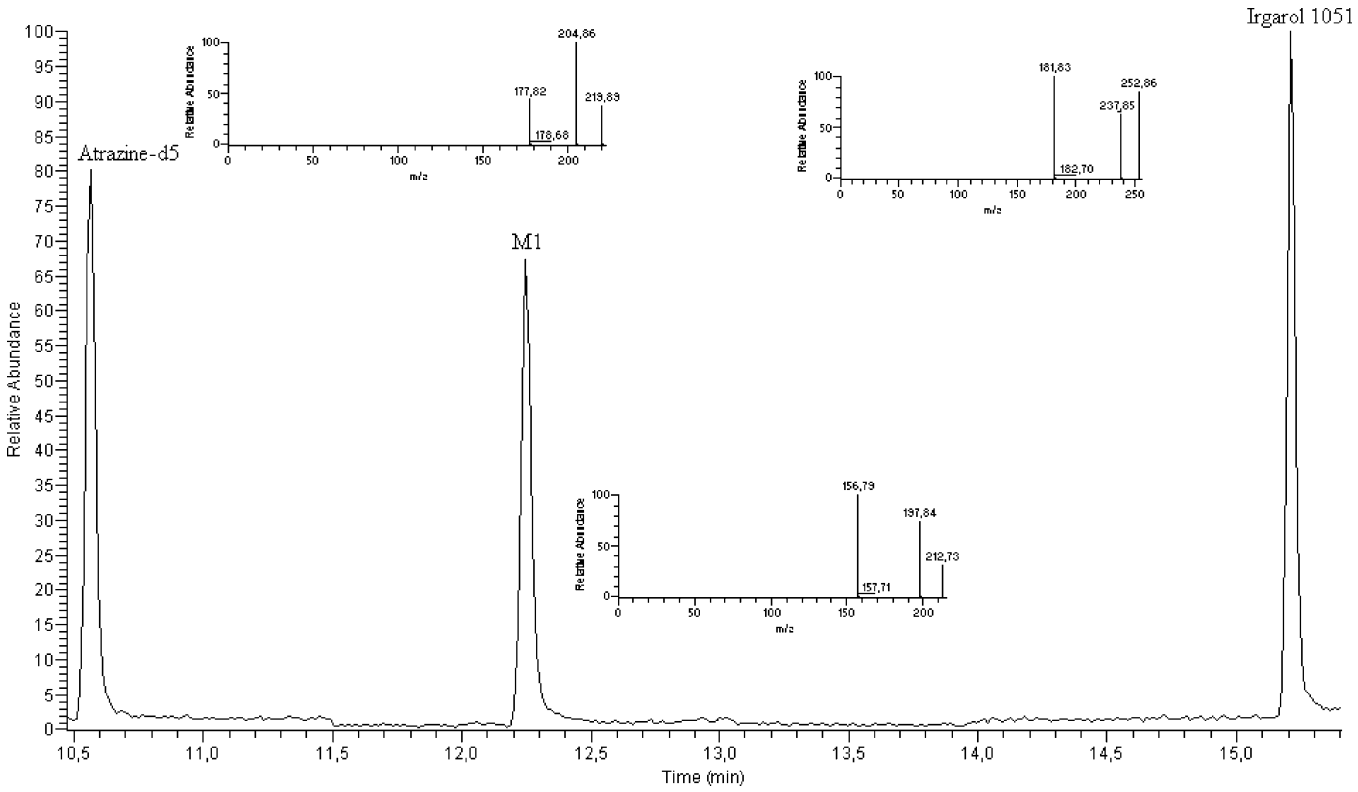

Fig. 1. Chromatogram of a standard solution containing 500 μg l^{-1} of the target compounds (Irgarol 1051 and M1) and the IS (atrazine-d_5) in SIM mode and their mass spectra.

concentration. Atrazine-d_5 was present as internal standard at a concentration of 0.5 mg l^{-1} in every standard solution. Matrix-matched calibration curve was also prepared with the same concentrations in blank sediment extract to check any difference in sensitivity. The latter calibration curve was used for the validation experiments and quantification.

The LOD of each compound was determined as three times the standard deviation of the response of 10 independent replicate analyses of 3 g of blank sediment samples spiked with 100 ng of atrazine-d_5. Precision was assessed by performing repeatability and reproducibility experiments by analyzing six replicates of a sample during one day (n = 6, intra-day precision), spiked at a level of 100 ng of the target compounds and the surrogate and two replicates at three different days (n = 2, k = 3, inter-day precision), over a period of one week. In order to evaluate the trueness of the method, recovery experiments were performed. To accomplish this, a marine sediment sample (3 g) was spiked at three fortification levels (10, 100 and 1000 ng) for each compound.

3. Results and discussion

3.1. Optimization of the MAE procedure

The results from the optimization experiments are given in Tables 1–4 For all the tested conditions, satisfactory recoveries were observed for both compounds, ranging from 69 to 121%. The results obtained from this work are in general agreement with other studies regarding the extraction efficiency of triazine compounds from soil using MAE [3,8,10,27].

The increase of the sediment amount up to 5 g did not affect the recovery of M1 (Table 1). The recovery of this compound was decreased only when 10 g of sediment was extracted. Perhaps, this was due to the fact that the volume of the extraction solvent remained constant to 30 ml, although the mass of the sediment was increased. Thus, the wetting of the sediment was not sufficient to extract the compounds to a greater extent. For Irgarol 1051, an optimum amount of sediment to be extracted was observed to be around 3 g when the highest (107%) recovery of the compound was achieved. In all of the other cases, the recovery ranged from 82 to 87% with no statistically significant difference between them. From this set of experiments, 3 g of sediment was chosen as the amount of the matrix, which provided the best recoveries for both compounds.

The increase in water volume affected the recovery of M1 only when 40 ml of the extraction solvent was used (Table 2). The recovery of the compound was lower (78.7%) compared with the recoveries obtained when a smaller volume of water was used during the extraction. This might happen because of the insufficient stirring of the solvent during the extraction. Other researchers [28,29] reported this phenomenon as

Table 1
Mean recovery and R.S.D. (%, n = 3) of M1 and Irgarol 1051 after the extraction of various amounts of sediment with 30 ml of water by MAE for 3 min at 105 °C

Sediment amount (g)	Substance			
	M1		Irgarol 1051	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
1	98.6[a]	7.66	86.8	7.35
2	121	8.64	87.1	2.60
3	112	8.30	107[a]	4.31
5	117	2.17	82.0	15.6
10	86.6[a]	7.09	85.6	10.3

[a] Value(s) for which the optimized parameter statistically significant affected the recovery at P = 0.05 (L.S.D. test).

Table 2
Mean recovery and R.S.D. (%, n = 3) of M1 and Irgarol 1051 after the extraction of 1 g of sediment with various water volumes by MAE for 3 min at 105 °C

Water volume (ml)	Substance			
	M1		Irgarol 1051	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
10	115	8.46	95.4	12.6
15	89.2	6.12	79.5	14.8
25	94.4	10.5	80.5	16.7
30	98.6	7.66	86.8	7.35
40	78.7[a]	8.70	84.9	7.97

[a] Value(s) for which the optimized parameter statistically significant affected the recovery at P =0.05 (L.S.D. test).

Table 3
Mean recovery and R.S.D. (%, n = 3) of M1 and Irgarol 1051 after the extraction of 1 g of sediment with 30 ml of water by MAE at 105 °C for various time periods

Time (min)	Substance			
	M1		Irgarol 1051	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
3	98.6	7.66	86.8	7.35
5	110	13.6	110[a]	10.5
10	92.1	3.25	93.2	2.59
15	71.4[a]	15.0	96.3	7.56
20	68.8[a]	18.3	86.1	15.1

[a] Value(s) for which the optimized parameter statistically significant affected the recovery at P =0.05 (L.S.D. test).

Table 4
Mean recovery and R.S.D. (%, n = 3) of M1 and Irgarol 1051 after the extraction of 1 g of sediment with 30 ml of water by MAE for 3 min at various temperatures

Temperature (°C)	Substance			
	M1		Irgarol 1051	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
100	97.3	9.08	81.2	1.10
105	98.6	7.66	86.8	7.35
115	103	12.6	106[a]	3.42
120	97.3	19.4	86.3	0.79
130	105	5.36	80.1	9.77

[a] Value(s) for which the optimized parameter statistically significant affected the recovery at P =0.05 (L.S.D. test).

Table 5
Calibration equations, coefficients of correlation (R^2) and limits of detection of M1 and Irgarol 1051 in marine sediments

Compound	Standard calibration curve	R^2	Matrix-matched calibration curve	R^2	LOD (ng g^{-1} dry weight)
M1	$y = 2.30x - 0.036$	0.9995	$y = 2.67x - 0.044$	0.9995	0.9
Irgarol 1051	$y = 2.87x - 0.048$	0.9991	$y = 3.79x - 0.064$	0.999	1.7

Table 6
Precision data of the MAE procedure at a level of 100 ng of the target compounds

Compound	Intra-day precision, R.S.D. (%), $n = 6$	Inter-day precision, R.S.D. (%), $n = 2$, $k = 3$
M1	5.13	9.80
Irgarol 1051	6.51	8.00

well. The recovery of Irgarol 1051 was not affected by the increase of water volume. Recoveries higher than 79.5% were observed in all cases. From this set of experiments, 30 ml of water was selected as the best solvent volume for the MAE of the studied compounds.

The duration of the extraction procedure resulted in a statistically significant decrease on the recovery of M1 when the sediment was extracted for longer than 10 min (Table 3). The recovery was reduced from 92.1% at 10 min extraction to approximately 70% at 15 and 20 min. According to the literature, long extraction times can cause degradation of the thermolabile compounds [30]. Although M1 is not a labile compound at high temperatures, the results show that degradation of the compound probably can take place to some extent under MAE conditions. For Irgarol 1051, the increase of the extraction time from 3 to 15 min improved its recovery. Further increase in extraction time (20 min) was found to be problematic since the recovery of the compound was reduced from 96.3 to 86.1%. From this set of experiments, 10 min of extraction was chosen as the optimum duration of the procedure. Other authors also suggest that a duration of 10 min is sufficient for the extraction of organic or

Table 7
Mean recoveries and R.S.D. of M1 and Irgarol 1051 from 3 g of sediments spiked at various levels of the compounds

Compound	10 ng ($n = 5$)		100 ng ($n = 4$)		1000 ng ($n = 3$)	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
M1	85.4	8.08	95.7	11.2	103	5.73
Irgarol 1051	104	9.13	101	14.0	114	6.69

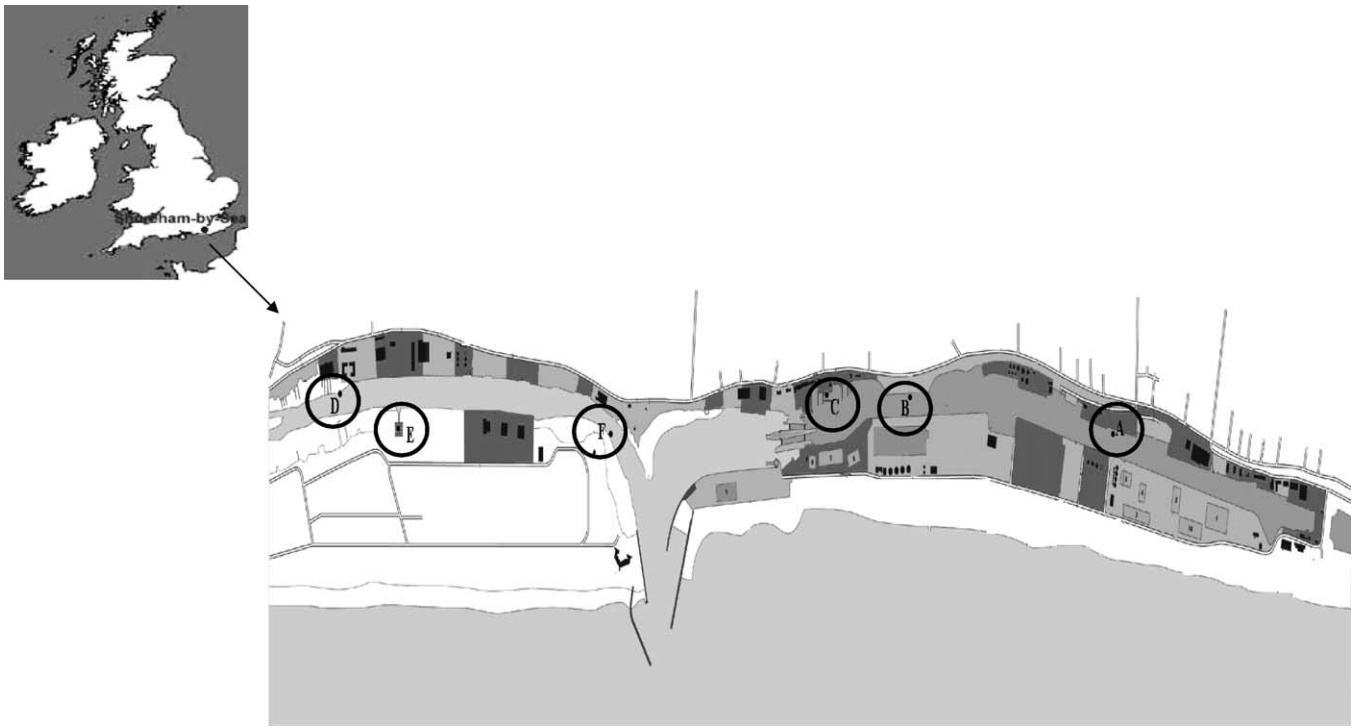

Fig. 2. Sampling sites around Shoreham Harbour. (A) Aldrington Wharf; (B) The Canal; (C) Lady Bee Marina; (D) Surry Boat Yard; (E) Emerald Quay and (F) Soldier Point.

organometallic compounds (e.g. PAHs, phenols, organochlorine pesticides, organotins) from soil and sediment [5,31].

The increase of temperature had no influence on the recovery of M1 (Table 4). While the temperature was increased from 100 to 130 °C, its recovery remained high (>97%). On the contrary, the recovery of Irgarol 1051 seemed to be affected by the increase of the extraction temperature. When the temperature was increased from 100 to 115 °C, the recovery was increased, reaching its highest value (106%). Further increase resulted in a decrease in the recovery of the compound (from 106% at 115 °C to 80.1% at 130 °C). It is worth noticing that the recovery was the same at the lowest and the highest temperatures and also was the same at the other two temperatures indicating that there is only one intermediate temperature from 100 to 130 °C, which provides best extraction efficiency for this compound.

The optimized procedure (3 g of sediment spiked with 100 ng of each compound extracted with 30 ml of water at 115 °C for 10 min) was repeated in triplicate to confirm the optimization results and satisfactory recoveries for both compounds were obtained. Recoveries were found to be 93.1 and 94.1% for M1 and Irgarol 1051, respectively, with R.S.D. less than 10% (2.70% for M1 and 7.09% for Irgarol 1051). The recoveries observed are in accordance with other studies regarding the microwave extraction of triazines from soils using water as the extraction solvent [3,10].

3.2. Validation of the method

This is the first time that MAE and GC–MS are used together for the simultaneous determination of Irgarol 1051 and its degradation product M1 from marine sediments. The method developed should be thoroughly evaluated. Calibration equations, coefficients of correlation (R^2) and limits of detection of M1 and Irgarol 1051 are given in Table 5. A slight increase in the response (peak area) of both target compounds was observed in the sediment extracts, but not in the response of atrazine-d_5. Therefore, matrix-matched calibration is preferred. The linear range is extended up to 2.5 mg l^{-1} for both compounds in the final solution, which means up to 0.25 μg g^{-1} in the sediment. The LODs obtained are low enough taking into account the small amount of the extracted sediment, and are sufficient for environmental monitoring.

The LODs of the target compounds obtained in this study are in the same range as or slightly better than those reported in other studies using MAE procedure for extracting triazinic compounds and their degradation products from soils [1,7,32]. Moreover, the LODs obtained in this study are slightly better than those obtained for both compounds in a previous study using HPLC–DAD [23] and in general are in the same order as those reported before for both compounds using LC–MS [22,24]. The previously reported LODs for the

Table 8
Comparison of the extraction procedure and efficiency of the various published methods for the determination of Irgarol 1051 in sediments. Recoveries of M1 are also reported where this compound was studied

Extraction method	Sediment mass	Solvent	Extraction time	Preconcentration/clean-up	Recovery (%)	Reference
Soxhlet	40 g ww	Acetone (n.s.[a] ml)	8 h	SPE (C18) + alumina + GPC	61	[14]
Mechanical agitation	20 g dw	3 × 50 ml hexane–acetone (85:15)	60 min	Florisil	103	[17]
	25 g dw	60 ml acetone + 50 ml DCM	Overnight	LLE: 3 × 30 ml petroleum ether	88	[18]
Sonication	5–10 g dw	3 × 10 ml DCM	n.s.[a]	–	95	[19]
	10 g ww	15 ml MeOH + 5 ml H_2O	30 min	SPE (C18)	90, 80 (M1)	[21]
	5 g dw	20 ml MeOH	30 min	SPE (Isolute ENV+)	69, 86 (M1)	[22]
	2 g dw	20 ml MeOH	30 min	SPE (C18)	86–103, 88–96 (M1)	[23]
Mechanical agitation + sonication	2 g dw	2 × (50 + 50) ml MeOH + ethylacetate	1 h + 10 min	–	99, 123 (M1)	[24]
	10 g ww	50 ml acetone	30 min + 30 min	LLE: 50 + 2 × 25 ml DCM + florisil	82	[25]
	5 g dw	30 ml H_2O–acetone (5%)	30 min + 30 min	SPME	67	[26]
	5 g dw	5 ml acetone	30 min + 30 min	SPME	92	[26]
SFE	4 g dw	CO_2/20% MeOH, TFA	30 min	Immunoaffinity column	87	[16]
MAE	3 g dw	30 ml H_2O	10 min	SPE (C18)	94–114, 85–103 (M1)	This work

[a] n.s.: not specified.

determination of Irgarol 1051 in sediments using GC–MS are in accordance with the LODs reported in this study, although the extracted mass of the sediment is higher in the previous studies [14,16,17,25,26].

Precision data of the extraction procedure are presented in Table 6. The results show satisfactory intra-day and inter-day precision of the analytical procedure with R.S.D. less than 10%, for both target compounds, indicating the good precision of the developed MAE procedure and the advantage of the applied internal standard method. Injection repeatability (as R.S.D., $n = 3$) was 2.3% for M1 and 1.0% for Irgarol 1051 of standard solutions containing 100 $\mu g\,l^{-1}$ of each compound and 5.7% for M1 and 4.2% for Irgarol 1051 of sediment extract containing 33 $ng\,g^{-1}$ of each compound (100 $\mu g\,l^{-1}$ in the final extract).

For the estimation of trueness, recovery experiments were performed at three fortification levels. The results obtained gave satisfactory recoveries for both compounds for all the fortification levels (Table 7). The obtained recoveries ranged from 85.4 to 114% with good reproducibility (R.S.D. $\leq$ 14%), indicating satisfactory isolation of the target compounds from the marine sediment with the MAE method developed. From the optimization and validation experiments it is evident that water is an efficient solvent for the extraction of Irgarol 1051 and M1 since it can easily absorb the microwave energy and transform it into thermal energy, thus increasing the solubility of the compounds in water. Moreover, water, as a polar solvent, can interact more effectively with the active sites on the surface of sediment where the target compounds are adsorbed, and promote their rapid desorption into the aqueous phase. The existing extraction procedures and their efficiency (given as recovery of Irgarol 1051 and M1) are compiled and compared with the results of this study in Table 8. Most of the studies reported adequate recoveries for Irgarol 1051, even if the extraction and clean-up methods varied. It is evident from Table 8 that there is a tendency of diminishing the use of organic solvents in the more recent studies [16,21–23,26] and the developed MAE method is the only one that uses pure water as the extractant. Moreover, MAE is faster than all the existing methods. Only four studies have reported recoveries for M1, three of which using ultrasonic agitation [21–23] and one combining mechanical and ultrasonic

Table 9
Concentration of the target compounds in marine sediment samples collected from Shoreham Harbor in the UK

Sampling site	Compound concentration ($ng\,g^{-1}$ dry weight)	
	M1	Irgarol 1051
Aldrington Wharf	7.4	9.2
The Canal	8.7	9.9
Lady Bee Marina	4.4	12
Surry Boat Yard	<LOD	2.5
Emerald Quay	4.1	3.2
Soldier Point	1.6	1.9

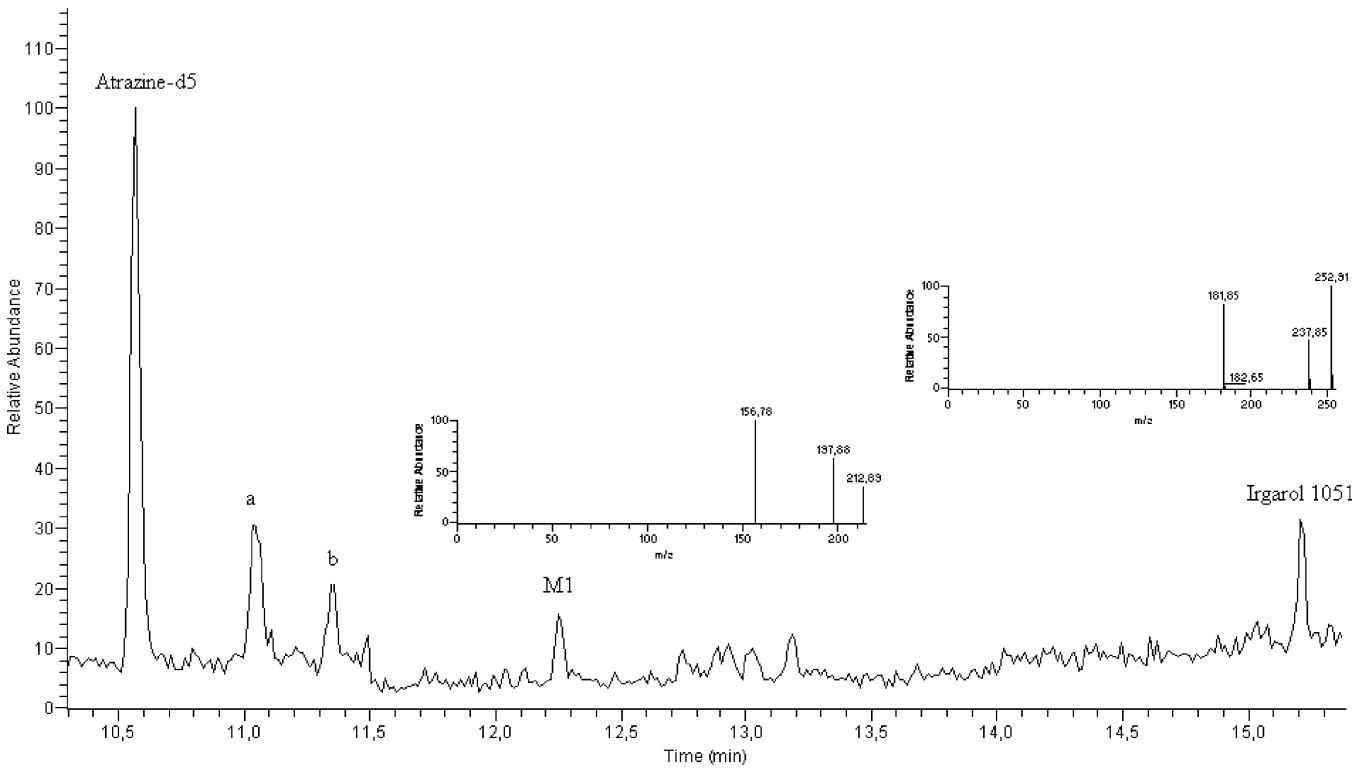

Fig. 3. Typical chromatogram of a marine sediment sample taken from the Lady Bee Marina (a and b, unknown compounds). SIM spectrum is given for M1 and Irgarol 1051.

agitation [24] showing similar extraction efficiencies to this work.

3.3. Application to natural samples

The optimum MAE method developed in this study was applied to marine sediments collected from six different sites in Shoreham Harbor in May 2003 (Fig. 2). Both compounds were present in most of the samples and their concentrations ranged from <LOD to 8.7 and <LOD to 12 ng g^{-1} for M1 and Irgarol 1051, respectively (Table 9). The concentrations of the compounds found are in accordance with the levels in marine sediments reported in other studies [15,16,21,25,33]. Typical chromatogram of an extract of a marine sediment sample taken from Lady Bee Marina is shown in Fig. 3. It is clear that the SIM–EI–MS spectrum of M1 in the sediment extract is identical with the mass spectrum of M1 standard solution (Fig. 1), with *m/z* 157 being the base peak. A similar EI–MS spectrum of M1 has been reported previously [34]. The SIM spectrum of Irgarol 1051 in the sediment extract, with *m/z* 253 being the base peak, followed by *m/z* 182 (85%) and 238 (48%), is somewhat different from the one produced from the Irgarol 1051 standard. This difference has been mentioned in the literature [35] and was attributed to the fact that the SIM–EI–MS spectra were obtained from different matrix solutions.

4. Conclusions

An efficient and accurate MAE method, followed by SPE GC–MS analysis, was developed for the determination of Irgarol 1051 and its main degradation product in marine sediments. Atrazine-d_5 was used as surrogate. Water was found to be a satisfactory solvent for the extraction of the target compounds. The use of water in MAE was preferred over the currently widely used organic solvents because it is safe, environmentally friendly and economic as a solvent and results in rapid extraction. In addition, solvent evaporation step is not required. The aqueous extract obtained can then be directly preconcentrated by a SPE procedure. The method can be utilized for the rapid determination of Irgarol 1051 and M1 from natural sediment samples. If high enough concentrations are expected, high performance liquid chromatography/mass spectrometry can be used directly after the MAE procedure, since water is a solvent compatible with this technique.

Acknowledgements

The authors would like to thank the CEFAS and Ciba-Geigy for the offer of M1. This work was funded by a Ph.D. Marie Curie fellowship (Georgia Gatidou) from the European Union 5th Framework Program (Contract No. HPMT-CT-2000-00181) and a Leverhulme Trust Research Grant to J.L. Zhou (Grant No. F/00230/H).

References

[1] R. Hoogerbrugge, C. Molins, R.A. Baumann, Anal. Chim. Acta 348 (1997) 247.
[2] C. Sparr Eskilsson, E. Björklund, J. Chromatogr. A 902 (2000) 227.
[3] G. Xiong, B. Tang, X. He, M. Zhao, Z. Zhang, Z. Zhang, Z. Zhang, Talanta 48 (1999) 333.
[4] I.J. Barnabas, J.R. Dean, I.A. Fowlis, S.P. Owen, Analyst 120 (1995) 1897.
[5] V. Lopez-Avila, R. Young, W.F. Beckert, Anal. Chem. 66 (1994) 1097.
[6] A. Pastor, E. Vázquez, R. Ciscar, M. de la Guardia, Anal. Chim. Acta 344 (1997) 241.
[7] G. Shen, H.K. Lee, J. Chromatogr. A 985 (2003) 167.
[8] G. Xiong, J. Liang, S. Zou, Z. Zhang, Anal. Chim. Acta 371 (1998) 97.
[9] S.J. Stout, A.R. daCunha, D.G. Allardice, Anal. Chem. 68 (1996) 653.
[10] T.R. Steinheimer, J. Agric. Food Chem. 41 (1993) 588.
[11] D. Liu, J.R. Maguire, L.Y. Lau, J.G. Pacepavicius, H. Okamura, I. Aoyama, Water Res. 31 (1997) 2363.
[12] H. Okamura, I. Aoyama, D. Liu, J.R. Maguire, J.G. Pacepavicius, L.Y. Lau, J. Environ. Sci. Health B 34 (1999) 225.
[13] D. Liu, J.G. Pacepavicius, J.R. Maguire, L.Y. Lau, H. Okamura, I. Aoyama, Water Res. 33 (1999) 155.
[14] S. Biselli, K. Bester, H. Hühnerfuss, K. Fent, Mar. Pollut. Bull. 40 (2000) 233.
[15] K. Haglund, A. Pettersson, M. Peterson, H. Kylin, S.C. Lord, P. Dollenmeier, Bull. Environ. Contam. Toxicol. 66 (2001) 50.
[16] P. Bou Carrasco, S. Díez, J. Jiménez, M.P. Marco, J.M. Bayona, Water Res. 37 (2003) 3658.
[17] S. Tóth, K. Becker-van Slooten, L. Spack, L.F. de Alencastro, J. Tarradellas, Bull. Environ. Contam. Toxicol. 57 (1996) 426.
[18] N. Voulvoulis, M.D. Scrimshaw, J.N. Lester, Chromatographia 50 (1999) 353.
[19] M.A. Gough, J. Fothergill, J.D. Hendrie, Mar. Pollut. Bull. 28 (1994) 613.
[20] H. Okamura, I. Aoyama, D. Liu, J.R. Maguire, J.G. Pacepavicius, L.Y. Lau, Water Res. 34 (2000) 3523.
[21] I. Ferrer, D. Barceló, J. Chromatogr. A 926 (2001) 221.
[22] K. Martinez, D. Barceló, Fresenius J. Anal. Chem. 370 (2001) 940.
[23] G. Gatidou, A. Kotrikla, N.S. Thomaidis, T.D. Lekkas, Anal. Chim. Acta 505 (2004) 153.
[24] K.V. Thomas, S.J. Blake, M. Waldock, Mar. Pollut. Bull. 40 (2000) 739.
[25] T.A. Albanis, D.A. Lambropoulou, V.A. Sakkas, I.K. Konstantinou, Chemosphere 48 (2002) 475.
[26] D.A. Lambropoulou, V.A. Sakkas, T.A. Albanis, J. Chromatogr. A 1010 (2003) 1.
[27] C. Molins, E.A. Hogendoorn, H.A.G. Heusinkveld, D.C. van Harten, P. van Zoonen, R.A. Baumann, Chromatographia 43 (1996) 527.
[28] K.K. Chee, M.K. Wong, H.K. Lee, Chromatographia 42 (1996) 378.
[29] B. Enders, G. Schwedt, GIT Fachz. Lab. 40 (1996) 172.
[30] K.K. Chee, M.K. Wong, H.K. Lee, J. Chromatogr. A 736 (1996) 211.
[31] O.F.X. Donard, B. Lalere, F. Martin, R. Lobinski, Anal. Chem. 67 (1995) 4250.
[32] Z. Vryzas, E. Papadopoulou-Mourkidou, J. Agric. Food Chem. 50 (2002) 5026.
[33] I.K. Konstantinou, T.A. Albanis, Environ. Int. 30 (2004) 235.
[34] G.A. Peñuela, I. Ferrer, D. Barceló, Intern. J. Environ. Anal. Chem. 78 (2000) 25.
[35] R.J.C.A. Steen, P.E.G. Leonards, U.A.Th. Brinkman, W.P. Cofino, J. Chromatogr. A 766 (1997) 153.