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Analytical methods for the determination of common booster biocides in marine samples

Review Article

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Abstract: Booster biocides are organic compounds that are added to antifouling copper-based paints to improve their efficacy. Due to their widespread use, they are common pollutants of marine ecosystems. Some of these compounds show acute and chronic toxic effects in non-targeted organisms at concentrations as low as ng L^{-1}. The determination of these compounds is therefore important, and for some, which are prioritized in the EU water framework directive, a necessity.

Because of their low concentrations and the matrix effect, these contaminants often require a suitable sample preparation step (extraction/pre-concentration) prior to chromatographic determination.

The aim of the present article is to review extraction and chromatographic methodologies related to the determination of common booster biocides in marine samples published in the scientific literature. These methodologies include liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME), single drop microextraction (SDME), Soxhlet extraction, microwave-assisted extraction (MAE), supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE) as extraction methods, and both gas and liquid chromatography as determination techniques.

Keywords: *Booster biocide • Irgarol 1051 • diuron • Sea nine 211*

1. Introduction

The term "biofouling" refers to the growth of undesirable organisms on submerged surfaces, such as vessel hulls. Biofouling can produce some negative consequences, such as increasing both fuel consumption and corrosion as well as the introduction of foreign species into new ecosystems [1]. Toxic compounds have been employed to avoid biofouling since sailing began [2]. Since the sixties, organotin compounds, such as tributyltin (TBT) or triphenyltin (TPT), have been used as antifoulants with good efficacy. Unfortunately, though, these compounds are highly toxic to non-targeted species such as gastropods and bivalves [3]. For this reason, the International Marine Organization (IMO) has released the International Convention on the Control of Harmful Antifouling Systems on Ships (AFS Convention), which are guidelines that forbid the use of these compounds [4]. The European Union established this convention as law with European Directive 782/2003 [5].

Paint manufacturers begin to employ copper components as cuprous oxide, copper thiocyanate (CuSCN) or metallic copper to replace the organotins as the principal antifouling compounds in their formulations, but these components are not effective for the full spectrum of fouling organisms and must be used in conjunction with other biocides [6]. The latter group of biocides are known as booster biocides and, in the past, were also added to TBT-based paints for large vessels [7]. Some are compounds which are frequently used as fungicides or herbicides in agricultural and industrial products. Table 1 shows some common booster biocides that are currently employed. Several studies have evaluated the toxicity of booster biocides on non-target species. Most of them are found to inhibit the growth of both fresh- and seawater autotrophs [8], which include key species such as seagrasses [9] or corals [10]. For example, diuron and Irgarol 1051, two of the most frequently used booster biocides, have toxic effects on the macrophytes and phytoplankton communities at the µg L^{-1} and ng L^{-1} levels [11]. These compounds both act through the same mechanism for their toxicity in autotrophic organisms, the inhibition of photosynthesis by blocking electron transport. Diuron and Irgarol 1051

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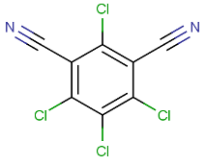
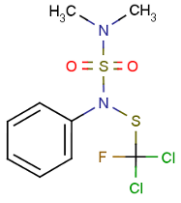
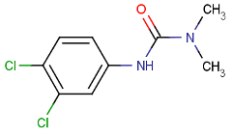
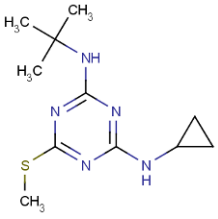
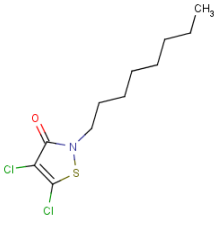
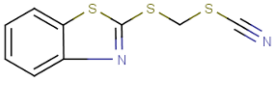
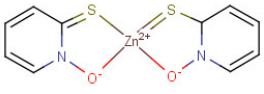
Table 1. Common booster biocides found in antifouling paints.

Compound	Molecular weight	Chemical structure	Log Kow	CAS Nº	Main degradation products
Chlorothalonil	265.91		2.64	1897-45-6	• Benzamide • Chloro-1,3-dicyanobenzene • Dichloro-1,3-dicyanobenzene • Trichloro-1,3-dicyanobenzene
Dichlofluanid	333.23		3.7	1085-98-9	• N,N-dimethyl-N'-phenyl-sulfamide (DMSA) • N-dichlorofluoromethylthion-aniline • Aniline • Dichlorofluoromethane
Diuron	233.09		2.85	330-54-1	• 1-(3-chlorophenyl)-3,1-dimethylurea (CPDU) • 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) • 1-(3,4-dichlorophenyl)urea (DCPU) • 3,4-dichloroanaline (DCA) • N-(3-chlorophenyl)-N-methylurea (mCPMU)
Irgarol 1051	253.37		2.38	28159-98-0	• 2-methylthio-4-tert-butylamino-6-amino-s-triazine (M1) • 3-[4-tert-butylamino-6-methylthiol-s-triazin-2-ylamino]-propionaldehyde (M2) • N,N'-di-tert-butyl-6-methylthiol-s-triazine-2,4-diamine (M3)
Sea nine 211 (4,5-dichloro-2-octyl-thiazol-3-one)	282.23		2.85	64359-81-5	• N-(n-octyl) malonamic acid • N-(n-octyl) nydroxypropionamide • N-(n-octyl) acetamide • N-(n-octyl) oxamic acid • N-(n-octyl) carbamic acid
TCMTB (2-(thiocyana-tomethyl thio) Benzothiazole)	238.35		3.3	21564-17-0	• 2-mercaptobenzothiazole (MBT) • Benzothiazole (BT) • 2-(methylthio)benzothiazole (MTBT)
Zinc pyrithione	317.69		0.97	154592-20-8	• 2-pyridine sulphonic acid

have been measured at concentrations of 2190 and 1000 ng L^{-1}, respectively, in Spanish coastal waters [12,13], and similar concentrations have also been found in other countries [14]. These concentration levels may be sufficient to affect the photosynthetic efficiency of ecologically important species, such as *Zostera marina* [9]. Futhermore, both booster biocides (diuron and Irgarol 1051) show little degradation in the marine medium during laboratory experiments. A half-life of 350 days has been established for Irgarol 1051 in sea water while diuron did not show any signs of degradation [15]. For these reasons, some countries, including the UK, Denmark and Sweden, have limited or prohibited the use of some booster biocides [16]. Moreover, diuron was included in the list of priority substances in the field of water policy and amending Directive 2000/60/EC of European Community [17].

At the beginning of the 1990s, no reliable data existed relating to the potential toxicity, characteristics or distribution of booster biocides in the marine environment, and this lack of knowledge motivated many studies in this field. For example, the project titled "Assessment of Antifouling Agents in Coastal Environments (ACE)", supported by the EU [18], contributed greatly to the field through its numerous publications. The principal drive of this project was the development of analytical methodologies for the determination of booster biocides in the marine environment.

Common booster biocides have been determined by gas chromatography (GC) coupled to several detectors, such as a flame thermionic detector (FTD) [19] or electron capture detector (ECD) [20]. However, in the last decade, liquid chromatography (LC) coupled to mass spectrometry, using ion trapping (IT) [21] and single [22] or triple quadrupole (QqQ) [23] detectors, has been effectively applied to the determination of these compounds. Measurement of the low concentrations found in marine environments, however, requires extraction procedures that achieve high degrees of pre-concentration.

In the present paper, we review methodologies optimized for the determination of common booster biocides in marine samples, such as sea water, sediment and biological samples. We discuss and compare the extraction-pre-concentration and clean-up techniques used in the determination systems employed to date.

2. Sample preparation

Frequently booster biocides are present at trace levels in marine environment. Consequently the extraction techniques that are used for their determination require a high degree of pre-concentration. Most methodologies that have been employed to date for water samples involve either a liquid-liquid extraction (LLE) or a solid phase extraction (SPE) with the objective of achieving limits of detection (LOD) on the order of ng L^{-1} or lower. Nevertheless, it is possible to find alternative extraction techniques for common booster biocides in the literature. We discuss the different methodologies for extraction and pre-concentration of booster biocides in both liquid and solid samples.

2.1. Sea water

Despite its well-known drawbacks, such as the high consumption of organic solvents and long analysis time, LLE is still used. For example, toluene has recently been employed as extractant for the determination of dichlofluanid, chlorothalonil and Irgarol 1051 in sea water samples from several harbours on the Korean coast [24]. However, the organic solvent most frequently employed in LLE is dichloromethane. This solvent has been used for the determination of both Irgarol 1051 [25-27] and its principal degradation product (M1, 2-methylthio-4-*tert*-butylamino-6-amino-s-traizine) [28-30] as well as for other booster biocides. Voulvoulis *et al.* [31] optimized a method for the determination of diuron, Irgarol 1051, chlorothalonil and dichlofluanid in estuarine waters using LLE with dichloromethane and achieving recoveries ranging from 90 to 96%. N-hexane [32] and an ethyl acetate:hexane (3:2) mixture [33] have also been employed for the concurrent determination of Irgarol 1051 and organotin compounds.

Multi-component methods are not often used for the determination of zinc pyrithione beacuse of the complexity of its analysis. Zinc pyrithione interacts with the reverse-phase packing materials or stainless steel components used in high performance liquid chromatography (HPLC) systems. Thomas [34] developed a method for the determination of zinc pyrithione making use of transchelation to the more stable copper pyrithione in association with LLE using dichloromethane. The LOD achieved was 20 ng L^{-1} while a recovery of 77% was obtained.

SPE has several advantages over LLE that make it suitable for the determination of booster biocides in water samples. Among these advantages are a lower consumption of organic solvents, a large variety of commercially available solid phases and formats, easy automation and reduced cost. Its principal drawback is that the frits can be blocked by particulate matter, making it necessary to filter samples before extraction. Common solid phases employed include C_{18} bonded silica [14,15,23,35-38], graphitized carbon black (GCB) [12] and polymeric materials such as poly(*N*-vinylpyrrolidone-divinylbenzene) copolymer (PVP-DVB, Oasis HLB) [13,39-42], polystyrene-divinylbenzene copolymer (PS-DVB, LiChrolut EN) [22,43,44], hydroxylated polystyrene-divinylbenzene (PS-DVB-OH, Isolute ENV+) [45-47] and methacrylate-divinylbenzene (MA-DVB, Excelpak SPE-GLF) [48] as well as more specific ones such as Isolute Triazine [49,50] and Envirelut Herbicide [51,52] or Pesticide [53]. Gatidou *et al.* [54] conducted a study that compared PS-DVB polymeric materials with C_{18} bonded silica cartridges for the extraction of diuron, Irgarol 1051 and some of their metabolites. Similar results were obtained for both solid phases with all analytes except 3,4-dichloroaniline (DCA, a degradation product of diuron), which had a low recovery using C_{18} cartridges (<35%). Despite this result, the authors opted to use C_{18} as the solid phase during the analysis of real samples because of its lower cost. Another study, conducted

by Martínez *et al.* [12], compared PS-DVB polymeric materials with GCB for the solid phase extraction of six common booster biocides (dichlofluanid, chlorothalonil, diuron, 2-(thiocyanatomethyl thio) benzothiazole - TCMTB, Irgarol 1051 and Sea nine 211) and two of the degradation products of diuron and one of Irgarol 1051 from sea water; good recoveries (76-96%) were obtained when the GCB phase was employed, but it was necessary to use 18 mL of a dichloromethane-methanol (8:2) mixture followed by 2 mL of methanol to elute all of the analytes. Polymeric materials showed poor recovery values for dichlofluanid, chlorothalonil and TCMTB (< 55%), although the analytes were effectively eluted by 6 mL of methanol. It was concluded that polymeric materials are suitable for the determination of Sea nine 211, Irgarol 1051, diuron and some of their degradation products.

Occasionally, the low recoveries obtained for certain booster biocides, such as dichlofluanid, chlorothalonil or TCMTB, by the SPE process are not due to the solid phase employed, but to the evaporation step of the extraction [12,44]. This drawback has been overcome by using cartridges with low polymeric mass that allows elution of the analytes using a small volume (1 mL) of an organic solvent (methanol) compatible with the mobile phase employed in HPLC [55,56]. On the other hand, the preservation of the sample may be a critical step towards adequately quantifying dichlofluanid, which degrades to *N'*-dimethyl-*N*-phenyl-sulphonamide (DMSA) at the pH of sea water [57] with a half-life of 18 h [16], and leading to a recommendation to acidify the sample to a pH<4 [58].

With respect to zinc pyrithione, Grunnet *et al.* [59] proposed the direct determination of the compound by extraction with Strata X cartridges (surface modified styrene-divinylbenzene polymer) and HPLC, and obtained a recovery of 85%.

In addition to the conventional cartridge format, it is possible to use extraction disks for SPE. The main advantage of these disks is their higher flow rate and, thus, shorter analysis time. C_{18} disks [19] have been used to determine chlorothalonil, dichlofluanid, Irgarol 1051 and Sea nine 211 with recoveries greater than 80%, except for dichlofluanid (56%). Polymeric disks [58,60] have also been used for the determination of dichlofluanid and DMSA with recoveries greater than 70% in both cases.

Some authors have also optimized on-line SPE procedures for the determination of booster biocides in sea water. Pocurull *et al.* [61] coupled SPE to gas chromatography-mass spectrometry (GC-MS) to determine Irgarol 1051, dichlofluanid and 4-chloro-3-methylphenol from 10 mL of sea water and obtained LODs between 10 and 20 ng L^{-1} and recoveries greater than 65%. Larger sample volumes could not be employed because of the decrease in recovery of 4-chloro-3-methylphenol. However, the SPE on-line procedure has also been used with liquid chromatography-mass spectrometry (LC-MS) [62-63]. Gimeno *et al.* [62] obtained LOD ranging from 5 to 20 ng L^{-1} for some of the booster biocides from a 100 mL sample of sea water with over 85% recovery using the on-line SPE-LC-MS methodology.

To reduce the required time and volume of organic solvents, some authors have used either solid phase microextraction (SPME) or single drop microextraction (SDME). Commonly, optimized methods where miniaturized extraction techniques are involved, such as SPME, involve immersing the fibre in the sample, but it is also possible to expose the fibre in the headspace of the sample at high temperature. Lambropoulou *et al.* [20] developed a method for the determination of Irgarol 1051 and Sea nine 211 from natural waters through headspace-solid phase microextraction (HS-SPME) with greater than 80% recovery using a polydimethylsiloxane-divinylbenzene (PDMS-DVB) fibre. A few studies have evaluated the methods optimized for coated fibres such as polyacrylate (PA) [64-67], polydimethylsiloxane (PDMS) [65,67], PDMS-DVB [64,65] and carbowax-divinylbenzene (CW-DVB) [64-65]. Konstantinou *et al.* [67] compared SPE with SPME for the extraction of chlorothalonil, dichlofluanid, Sea nine 211 and Irgarol 1051 from different natural waters. C_{18}, PS-DVB and GCB disks were employed in the SPE while PA and PDMS fibre coatings were employed in the SPME. Adequate recoveries (>75%) were obtained through SPE for all samples except dichlofluanid (≤65%), for the C_{18} and PS-DVB disks, and chlorothalonil (<60%), for the GCB disks whereas ≥65% recovery was achieved for SPME by both coated fibres.

SDME is an extraction technique based on the pre-concentration of the sample into a single drop of organic solvent (1-2 µL). It offers the advantages of simplicity, fast analysis, and easy automation. Lambropoulou *et al.* [68] evaluated the applicability of this technique to the determination of chlorothalonil, dichlofluanid and Sea nine 211 from tap, river and sea waters using toluene as the solvent. The recoveries obtained ranged from 78 to 104%.

Finally, passive sampling devices have been employed to quantify booster biocides. Passive sampling techniques allow for the time integrated extraction of these pollutants from water. Depending on the surface area and uptake resistances, samplers extract analytes at a predetermined sampling rate, which is measured as litres sampled per day submerged in the medium. Shaw

et al. [69] used a sulfonated styrene-divinylbenzene copolymer (SDB-RPS, Empore disk) for the extraction of photosystem II inhibitor herbicides, such as diuron or Irgarol 1051, from the sea waters of Hong Kong. The sampling rate of the disks was estimated to be 0.6 litres per day.

Screening techniques, such as enzyme-linked immunosorbent assay (ELISA), have also been employed. The main advantage of ELISA is fast analysis, but it is subject to interference, and confirmatory analyses could be necessary. Ferrer *et al.* [70] achieved a LOD of 20 ng L^{-1} for the determination of Irgarol 1051 by means of an ELISA procedure. This method was satisfactory for application to real samples and detecting the presence of Irgarol 1051. In a different approach, Bou Carrasco *et al.* [71], employed an ELISA for the determination of Irgarol 1051 after the extraction and pre-concentration of the sample using immunoaffinity chromatography (IAC), which utilizes the antibody-antigen interaction to immobilize analytes in the same way as in SPE. By means of IAC, the authors achieved a LOD twenty times lower than that of the C_{18} cartridge.

2.2. Sediment samples

Less attention has been given to sediment samples because most analytical methods have been developed for water samples. Many methods employed to determine booster biocides in sediments are based on conventional techniques, such as Soxhlet extraction, mechanical shaking [31,48,58,60,72-76], sonication [35,77-80] or both mechanical shaking and sonication [81,82]. Biselli *et al.* [36] optimized a method for determination of Irgarol 1051 by means of Soxhlet extraction with acetone, to obtain a recovery of 61%. In addition, Ferrer *et al.* [83] employed methanol as the solvent for the Soxhlet extraction, immunosorbent pre-concentration and on-line LC analysis for the determination of pesticides (phenylureas and triazines) in sediments. Among solvents employed for mechanical shaking and sonication, those most frequently used have been dichloromethane [35,84], acetone [58,60,78,81], n-hexane:acetone [76], acetonitrile [48,72-75,77], acetone:dichloromethane [31], methanol [79,80], and metanol:ethyl acetate [82].

Nevertheless, conventional techniques require a large volume of organic solvents, consume a significant amount of time and involve numerous steps, which makes them environmentally unfriendly, tedious and costly. For these reasons, alternative extraction techniques have been optimized in the last decade for the determination of common booster biocides from marine sediment samples. These more recent techniques include microwave assisted extraction (MAE) [85-87], supercritical fluid extraction (SFE) [88] and pressurized liquid extraction (PLE) [42]. MAE consists of the absorption of microwave energy by the extraction solvents to increase their temperature and pressure. Gatidou *et al.* [85] optimized a method for the determination of Irgarol 1051 and its main degradation product (M1) by means of MAE with water as the solvent. A SPE step was used for pre-concentration and to change the solvent to one suitable for GC. The recoveries achieved ranged from 85.4 to 114%. Other authors have employed methanol [86] and n-hexane:acetone (1:1, v/v) [87] as solvents for MAE to determine common booster biocides and obtained recoveries greater than 75 and 70%, respectively.

SFE is based on the high solvent power of supercritical fluids. Bou Carrasco *et al.* [88] employed CO_2-methanol as a supercritical fluid for the determination of Irgarol 1051 and obtained up to 95% recovery. Finally, PLE is similar to Soxhlet extraction except that the extraction is carried out at high pressure, which prevents the solvent from boiling. Dichloromethane:acetone (1:1, v/v) has been employed as the solvent for determining diuron and Irgarol 1051 from marine sediments and obtained recoveries ranging from 51 to 84% [52]. Other solvents mixtures, including methanol:water (4:1, v/v) [42], have also been used in the PLE of some herbicides, such as diuron.

After sediment extraction, a clean-up step is frequently employed to remove interferences and pre-concentrate the analytes. This clean-up step is commonly performed using SPE with Florisil (activated magnesium silicate) [76,81,84,87], Oasis HLB [42,77], C_{18} [78,80,85], Insolute ENV+ [79] or Envirelut Pesticide [86] as the solid phase. However, other extraction techniques, such as SPME [89] or IAC [88], can be employed for clean-up.

Methods optimized for the determination of booster biocides in sediment samples can also be used to determine their concentration in paint particles that can be present in sediment samples from harbours and shipyards. Some studies have focused on the presence of biocides in these particles and used LLE with either mechanical shaking with a methanol:ethyl acetate mixture as the solvent [90] or sonication in dichloromethane [91].

2.3. Biological samples

A small number of papers are focused on booster biocide determination in biological samples. Frequently, these studies employ the same methods used to determine the analytes in sediments [76,78]. Conventional techniques, such as Soxhlet extraction with acetone:dichloromethane (1:1, v/v), have been used for the determination of Irgarol 1051 from seagrass samples with over 97%

recovery [92,93]. Extraction by mechanical shaking with n-hexane:acetone (1:1, v/v) has also been used for the determination of some pesticides and herbicides, including diuron in seagrass samples from the Great Barrier Reef (Australia) [94]. In addition, the extraction of booster biocides from bivalves has been carried out using mechanical shaking with acetonitrile as solvent with recoveries ranging from 63 to 92% from mussels [74] and from 60 to 99% from clams [73] for diuron, dichlofluanid, Irgarol 1051, M1 and Sea nine 211. Rencently, for determination of zinc pyrithione from mussel samples, dichloromethane has been employed as solvent in conjunction with transchelation to copper pyrithione (making use of copper nitrate) with a recovery of 96% [95].

Table 2 summarizes the methods employed for the extraction and determination of booster biocides in marine matrices.

3. Chromatographic determination

3.1. Gas chromatography

Gas chromatography is a suitable technique for the separation and determination of common booster biocides, such as chlorothalonil, dichlofluanid, Irgarol 1051, Sea nine 211 and TCMTB. Diuron is thermolabile and frequently determined by LC, although it can also be determined using GC after a derivatization process. Voulvoulis *et al.* [31] optimized a method for determination of diuron by GC after methylation with trimethylanilinium hydroxide (TMPAH, MethElute reagent).

The chromatographic resolution of these compounds can usually be achieved with common, nonpolar GC capillary stationary phases, such as methylpolysiloxane or phenyl-methylpolysiloxane, and grading from temperatures of 60-80ºC up to 280-320ºC [7]. A splitless injection mode is the most commonly employed because of its robustness, although on-column [27,61,96] and programmable temperature vaporization (PTV) [97] have been also used. A typical volume injected in splitless mode is 2 µL, although Agüera *et al.* [40] optimized a method to inject a larger sample volume (10 µL) by means of electronic pressure programming (EPP), which increased the signal × 4 with respect to the conventional, 2 µL, splitless injection. EPP permits the programmed elevation of the column head pressure to avoid poor peak shapes and tailing. Classic GC detectors, such as electron capture detector (ECD) [19,20,65], flame thermionic detector (FTD) [19,64], flame ionization detector (FID) [26], alkali flame ionization detector (AFID) [36] and nitrogen phosphorous detector (NPD) [26,71,87,88,98], have been used for the determination of booster biocides. Nevertheless, mass spectrometry (MS) detectors are most frequently used to determine the concentration of these compounds in environmental samples. They provide unambiguous component identification and achieve a greater sensitivity in the selected ion monitoring (SIM) and tandem (MS/MS) modes. IT [84] and quadrupole [81] detectors are the mass spectrometry detectors most commonly coupled to GC, while electron impact ionization (EI) and chemical ionization (CI) with methane as the reagent gas are the predominant ion sources. For chlorothalonil, dichlofluanid, Sea nine 211 and TCMTB, negative chemical ionization (NCI) has shown greater sensitivity than EI. However, the absence of spectral libraries for CI as well as poor fragmentation and sensitivity for Irgarol 1051 [40,41] makes EI the preferred ionization mode of most authors.

Fig. 1 shows the ion current GC–MS chromatogram of selected herbicides and booster biocides.

3.2. Liquid chromatography

Despite the common use of GC for booster biocide determination, LC with absorbance detection using a diode array detector (DAD) has traditionally been employed to determine diuron. In some studies, DADs have been used to determine diuron conjointly with other booster biocides and degradation products [54,70,80].

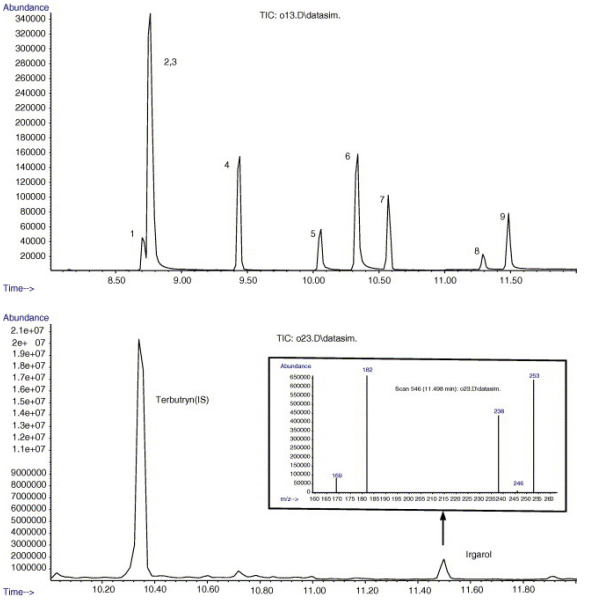


Figure 1. Total ion current GC–MS chromatograms of selected herbicides and booster biocides (1 = simazine; 2 and 3 = atrazine and atrazine D5, respectively; 4 = chlorothalonil; 5 = ametryn; 6 = terbutryn; 7 = dichlofluanid; 8 = Sea nine 211; and 9 = Irgarol 1051) as well as an extract from a sea water sample that shows the presence of Irgarol 1051 (8 ng L^{-1}). Chromatogram is taken from [50].

Table 2. Methods for the extraction and determination of common booster biocides in liquid and solid samples.

Compounds	Matrix	Sample pretreatment	Extraction technique	Characteristics	Instrumental analysis	Analytical parameters	Ref.
Irgarol 1051 and M1	Sea water	0.45 μm filtered	LLE	Dichloromethane	GC-MS (SIM)	MDLs: 0.6-0.7 ng L^{-1}	[29]
Chlorothalonil, dichlofluanid and Irgarol 1051	Sea water	-	LLE	Toluene	GC-MS (SIM)	Recoveries: 73.6-120.3 % RSDs: 1.6-4.9 % LODs: 1.8-7.7 ng L^{-1}	[24]
Chlorothalonil, dichlofluanid, diuron and Irgarol 1051	Estuarine water	-	LLE	Dichloromethane	GC-MS (SIM)	Recoveries: 90-96 % RSDs: 2-7 % LODs: 150-240 ng L^{-1}	[31]
Chlorothalonil, dichlofluanid, Irgarol 1051 and Sea nine 211	Sea water	pH< 3 H_2SO_4, Methanol	SPE	C_{18} disks	GC-FTD, ECD and MS(SIM)	Recoveries: 56-93% RSDs: 2-11% LODs: 0.42-95 ng L^{-1}	[19]
Diuron, IPBC, Irgarol 1051, M1, Thiabendazole and Sea nine 211	River and sea waters	-	SPE	MA-DVB (Excelpak SPE-GLF)	LC-MS/MS (MRM)	Recoveries: 72-97 % RSDs: 6.5-15.0 % IDLs: 0.3-1.9 ng L^{-1}	[48]
Dichlofluanid, diuron, Irgarol 1051 and TCMTB	Sea water	0.65 μm filtered	SPE	Envirelut Pesticide	LC-MS/MS (MRM)	Recoveries: 72.8-100.6 % RSDs: 2.5-8.3 % LODs: 0.1-0.2 ng L^{-1}	[56]
Chlorothalonil, dichlofluanid, diuron, Irgarol 1051, TCMTB, Sea nine 211 and the degradation products of Irgarol 1051 and diuron	Sea water	0.45 μm filtered	SPE	GCB (ENVI-Carb), PS-DVB (LiChrolut EN and Isolute ENV+)	LC-MS (SIM)	Recoveries: 8-105 % LODs: 2-20 ng L^{-1}	[12]
Dichlofluanid, diuron and Irgarol 1051	Sea water	0.45 μm filtered, pH= 3 acetic acid	SPE	PS-DVB (LiChrolut EN)	LC-MS (SIM)	Recoveries: 56-96 % RSDs: 3-14 % LODs: 0.2-0.9 ng L^{-1}	[44]
Diuron, Irgarol 1051 and degradation products	Sea water	0.7 μm filtered	SPE	C_{18} (Sep-Pak) and PS-DVB (Envi-Chrom P and Isolute ENV+)	LC-DAD	Recoveries: 29-106 % RSDs: 2-10-14 % LODs: 6-26 ng L^{-1}	[54]
Diuron and Irgarol 1051	Sea water	0.45 μm filtered	SPE	PS-DVB (LiChrolut EN)	LC-MS/MS (MRM)	Recoveries: 77-93 % RSDs: 2.3-7.4 % LODs: 0.2-0.5 ng L^{-1}	[43]
Chlorothalonil, dichlofluanid, Irgarol 1051, TCMTB and Sea nine 211	Sea water	-	SPE	PVP-DVB (Oasis HLB)	GC-MS (Full Scan and SIM)	Recoveries: 42-98 % RSDs: 7-15 % LODs: 0.5-20000 ng L^{-1}	[40]
Chlorothalonil, dichlofluanid, Irgarol 1051, TCMTB and Sea nine 211	Sea water	-	SPE	PVP-DVB (Oasis HLB)	GC-MS/MS	Recoveries: 42-98 % RSDs: <15 % LODs: 0.05-50 ng L^{-1}	[13]
Diuron, Irgarol 1051 and M1	Sea water	-	SPE	C_{18}	LC-MS/MS (MRM)	Recoveries: 91-102 % RSDs: 5-8 % MDLs: 1-2 ng L^{-1}	[23]
Diuron, Sea nine 211, TCMTB and TCMS pyridine	Sea water	-	SPE	C_{18}	LC-MS (SIM)	Recoveries: 91.2-113.1 % RSDs: 10.0-20.1 % LODs: 1-5 ng L^{-1}	[21]
Irgarol 1051, dichlofluanid and 4-chloro-3-methylphenol	River and sea waters	Acidified acetic acid, 10 % Methanol	SPE-online	PS-DVB (PLRP-S column)	GC-MS (Full scan and SIM)	Recoveries: 69-84% RSDs: 5-23% LODs: 10-200 ng L^{-1}	[61]

Continued **Table 2.** Methods for the extraction and determination of common booster biocides in liquid and solid samples.

Compounds	Matrix	Sample pretreatment	Extraction technique	Characteristics	Instrumental analysis	Analytical parameters	Ref.
Chlorothalonil, dichlofluanid, Irgarol 1051, diuron and TCMTB	Sea water	0.45 μm filtered	SPE-online	C_{18} and PS-DVB (PLRP-S) columns	LC-MS (SIM)	Recoveries: 63-111% RSDs: 2-9% LODs: 2-10 ng L^{-1}	[63]
Folpet, dichlofluanid, diuron and Irgarol 1051	Sea water	0.45 μm filtered, pH= 3 acetic acid	SPE-online	PS-DVB (LiChrolut EN)	LC-MS (Full scan and SIM)	Recoveries: 85-99 % RSDs: 1-8 % LODs: 5-400 ng L^{-1}	[62]
Irgarol 1051 and Sea nine 211	River, lake and sea waters	-	SPME	PDMS, PA, PDMS-DVB and CW-DVB fibres	GC-FTD,ECD and MS(SIM)	Recoveries: 60-118% RSDs: 3-10% LODs: 2-60 ng L^{-1}	[64]
Irgarol 1051, dichlofluanid and 4-chloro-3-methylphenol	River and sea waters	0.45 μm filtered	SPME	PA fibre	GC-MS (Full scan and SIM)	RSDs: 13-26% LODs: 5-3000 ng L^{-1}	[66]
Irgarol 1051 and Sea nine 211	River, lake and sea waters	-	SPME-HS	PDMS-DVB	GC-FTD,ECD and MS(SIM)	Recoveries: 82-118% RSDs: 3-12% LODs: 2-30 ng L^{-1}	[20]
Chlorothalonil, dichlofluanid and Sea nine 211	Tap, river and sea waters	-	SDME	Toluene	GC-ECD	Recoveries: 78-104 % RSDs: 3.9-8.5 % LODs: 0.25-3 ng L^{-1}	[68]
Dichlofluanid and DMSA	Marine sediments	Sieved, pH<6 acetic acid	Mechanical shaking	Acetone	GC-MS (SIM)	Recoveries: 80-109 % RSDs: 4-10 % LODs: 3-10 ng g^{-1}	[60]
Diuron, Irgarol 1051 and M1	Marine sediments	Dried, ground and sieved	Mechanical shaking and sonication	Methanol:ethyl acetate (1:1, v/v)	LC-MS(SIM)	Recoveries: 99-123 % RSDs: 5.1-5.7 % LODs: 1-10 ng g^{-1}	[82]
Dichlofluanid, diuron, Irgarol 1051, Sea nine 211 and the degradation products of diuron and Irgarol	Marine sediments	Freeze-dried and sieved	Sonication	Methanol	LC-MS(SIM)	Recoveries: 54-109 % RSDs: 2-19 % LODs: 0.2-1.6 ng g^{-1}	[79]
Diuron, Irgarol 1051 and degradation products	Marine sediments	Sieved, dried and ground	Mechanical shaking and sonication	Methanol	LC-DAD	Recoveries: 34.6-106.4 % RSDs: 4.8-14.6 % LODs: 1.7-4.0 ng g^{-1}	[80]
Diuron, IPBC, Irgarol 1051, M1, Thiabendazole and Sea nine 211	Marine sediments	-	Mechanical shaking	Acetonitrile	LC-MS/MS (MRM)	Recoveries: 65-103 % RSDs: 7.5-14.0 % IDLs: 0.04-0.18 ng g^{-1}	[48]
Irgarol 1051 and degradation products	Marine sediments	Freeze-dried	Sonication	Acetone	LC-MS/MS (MRM)	Recoveries: 86.2-94.9 % RSDs: 1.4-4.0 % MDLs: 1.4-19.3 pg g^{-1}	[78]
Diuron and Irgarol 1051	Marine sediments	Dried	PLE	Dichloromethane: acetone (1:1, v/v)	GC-MS (SIM)	Recoveries: 51-84 % RSDs: 5.0-5.2 % LODs: 12-17 ng g^{-1}	[52]
Chlorothalonil, dichlofluanid, folpet, Irgarol 1051 and Sea nine 211	Marine sediments	Freeze-dried and sieved	MAE	Acetone:n-hexane (1:1, v/v)	GC-NPD	Recoveries: 70-93 % RSDs: <10 % LODs: 1-10 ng g^{-1}	[87]
Irgarol and M1	Marine sediments	-	MAE	Water	GC-MS(SIM)	Recoveries: 85.4-114 % RSDs: 5.7-14.0 % LODs: 0.9-1.7 ng g^{-1}	[85]
Dichlofluanid, diuron, Irgarol 1051 and TCMTB	Marine sediments	Freeze-dried, ground and sieved	MAE	Methanol	LC-MS/MS (MRM)	Recoveries: 76.1-99.7 % RSDs: 2.5-6.5 % LODs: 0.1-0.3 ng g^{-1}	[86]

Continued **Table 2.** Methods for the extraction and determination of common booster biocides in liquid and solid samples.

Compounds	Matrix	Sample pretreatment	Extraction technique	Characteristics	Instrumental analysis	Analytical parameters	Ref.
Irgarol 1051	Seagrasses	Mixed with Na_2SO_4	Soxhlet	Dichloromethane: acetone (1:1, v/v)	GC-MS (SIM)	Recoveries: 97% RSDs: 7.9 % LODs: 0.3 ng g^{-1}	[92]
Irgarol 1051 and degradation products	Mussels	Freeze-dried	Sonication	Acetone	LC-MS/MS (MRM)	Recoveries: 88.2-94.5 % RSDs: 0.5-3.9 % MDLs: 5.0-18.3 pg g^{-1}	[78]
Diuron, Irgarol 1051, M1 and Sea nine 211	Mussels	-	Mechanical shaking	Acetonitrile	LC-MS/MS (MRM)	Recoveries: 63-92 % RSDs: 4-7% LODs: 0.24-1.0 ng g^{-1}	[74]

Abbreviations: see Abbreviations

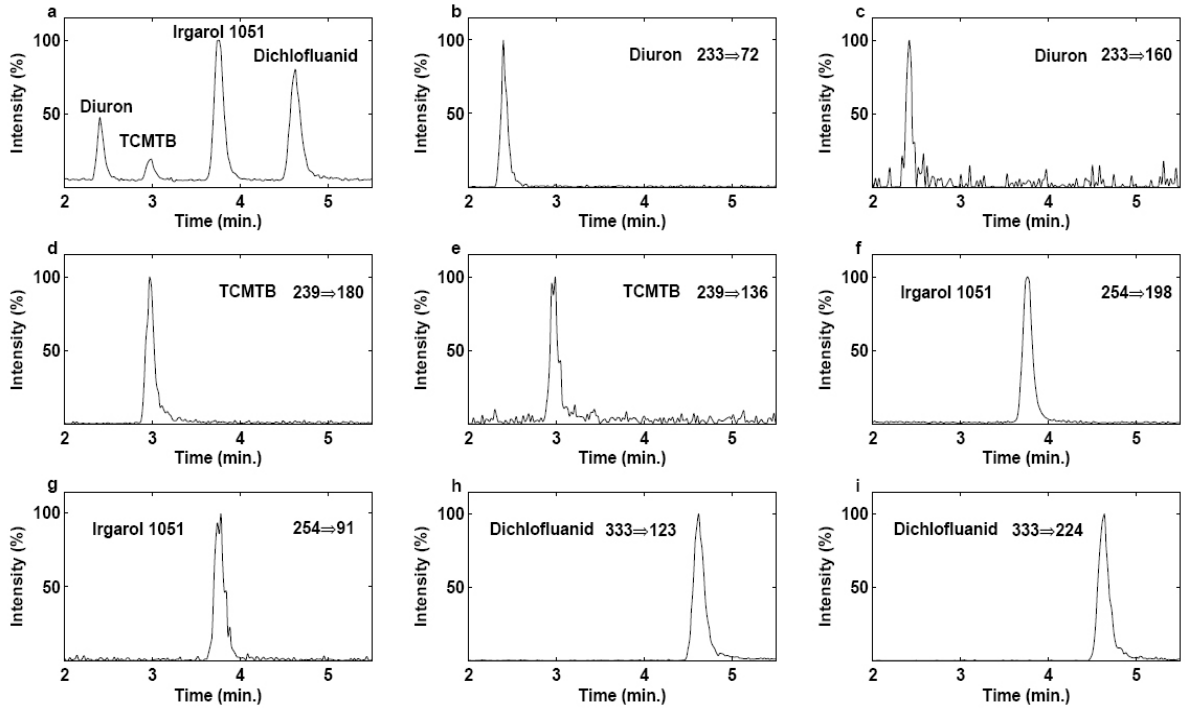


Figure 2. Total ion current (a) and selected ion (b-i) chromatograms obtained from a spiked seawater sample (10 ng L^{-1}) by LC-MS under MRM mode. Chromatogram taken from [56].

The identification of analytes by LC-DAD is accomplished by comparing the retention time and UV spectrum obtained. Nonetheless, the technical development of liquid chromatography mass spectrometry (LC-MS) in the last decade has allowed it to gain acceptance, and led to its widespread use for the determination of booster biocides in environmental samples. The use of MS detectors coupled to LC has achieved increased sensitivity of analysis and more discriminatory identification of analytes. The mass spectrometry detectors that have been commonly used are IT [21], single quadrupole [22], triple quadrupole [23] and, more recently, hybrid techniques such as triple quadrupole/linear ion trap [78]. The ionization techniques commonly employed in LC-MS are electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). Both negative ionization (NI) and positive ionization (PI) modes have been evaluated. Better sensitivity is achieved for chlorothalonil, dichlofluanid and TCMTB using NI whereas Irgarol 1051, diuron and Sea nine 211 are commonly determined using PI [12].

Reverse phase liquid chromatography (RPLC) is commonly used with an octadecyl stationary phase (C_{18}), although octyl columns (C_8) have also been used [63,70,99]. The stationary phase commonly used for booster biocide elution is composed of 5 µm particles, although smaller particles have also been used. Sánchez-Rodríguez *et al.* [56] optimized a method that employed a Varian Pursuit UPS 2.4 C_{18} column (50×2.0 mm, 2.4 µm particle size) set to 40ºC for the

chromatographic resolution of diuron, TCMTB, Irgarol 1051 and dichlofluanid in 5.5 min under an isocratic program. Fig. 2 shows an example of a total ion current (TIC) and selected ion chromatogram. The analytes are usually eluted with either methanol or acetonitrile mixed with water. The mobile phase is commonly modified with ammonium acetate, formic acid or ammonium formate to improve the ion production and MS detection.

4. Conclusions and future trends

Increased concern about the environmental impact of toxic antifouling paints has impelled the research and development of non-toxic alternatives, such as foul-release coatings that incorporate silicone elastomers, waxes or silicone oils [100]. Unfortunately, foul-release coatings are only effective for high speed (>15 knots) vessels in near-continuous service, and so for the near future, there will be a continuing need for antifouling paints based on biocides.

This review examines the alternatives employed to date for the determination of booster biocides in several matrices from the marine environment. The extraction techniques commonly used to determine these compounds in sea water are LLE and SPE, although other more recent extraction techniques such as SPME or SDME have been successfully applied. For solid samples, common procedures involve mechanical shaking, sonication or Soxhlet extraction, but other extraction procedures, such as MAE or PLE, have gained acceptance in the last decade. The determination of these compounds can also be achieved using GC or LC with standard stationary and mobile phases.

Future refinements in the extraction and determination of booster biocides will focus on the development of novel techniques that promise reduced consumption of organic solvents and faster analysis. In this regard, microextraction techniques such as solid phase microextraction (SPME), in-tube SPME, stir-bar sorptive extraction (SBSE), microextraction in packed sorbent (MEPS) or single drop microextraction (SDME) are more environmentally friendly than the classic techniques because less organic solvent is used. Adequate sensitivity can be obtained by coupling these novel extraction procedures with GC-MS/MS and LC-MS/MS instruments.

Automation of these procedures also offers advantages over the original techniques. Automated, on-line SPE, MEPS or SPME procedures can be coupled to ultra-high performance liquid chromatography (UHPLC) with mass spectrometry detection to reduce the analysis time, which increases the number of samples analysed and thus the productivity.

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Abbreviations

AFID: Alkali flame ionization detector;
APCI: Atmospheric pressure chemical ionization;
CI: Chemical ionization;
CW-DVB: Carbowax-divinylbenzene;
DAD: Diode array detector;
DCA: 3,4-dichloroaniline;
DMSA: *N'*-dimethyl-*N*-phenyl-sulphonamide;
ECD: Electron capture detector;
EI: Electron impact ionization;
ELISA: Enzyme-linked immunosorbent assay;
EPP: Electronic pressure programming;
ESI: Electrospray ionization;
FID: Flame ionization detector;
FTD: Flame thermionic detector;
GC: Gas chromatography;
GCB: Graphitized carbon black;
GC-MS: Gas chromatography-mass spectrometry;
HPLC: High performance liquid chromatography;
HS: Head space;

IAC: Inmunoaffinity chromatography;
IDL: Instrumental detection limit;
IMO: International Marine Organization;
IPBC: 3-Iodo-2-propynyl butylcarbamate;
IT: Ion trap ;
LC: Liquid chromatography;
LC-MS: Liquid chromatography-mass spectrometry;
LLE: Liquid-liquid extraction;
LOD: Limit of detection;
M1: 2-methyl-thio-4-*tert*-butylamino-6-amino-s-traizine;
MA-DVB: Methacrylate- divinylbenzene;
MAE: Microwave assisted extraction;
MDL: method detection limit;
MEPS: Microextraction in packed sorbent;
MS/MS: tandem mass spectrometry;
MS: Mass spectrometry;
NCI: Negative chemical ionization;
NI: Negative ionization;
NPD: Nitrogen phosphorous detector;
PA: Polyacrylate;
PDMS: Polydimethylsiloxane;
PDMS-DVB: Polydimethylsiloxane-divinylbenzene;
PI: Positive ionization;
PLE: Pressurized liquid extraction;
PS-DVB: Polystyrene-divinylbenzene;
PS-DVB-OH: Hydroxylated polystyrene-divinylbenzene;
PTV: Programmable temperature vaporization;
PVP-DVB: Poly(*N*-vinylpyrrolidonedivinylbenzene) copolymer;
QqQ: Triple quadrupole;
RPLC: Reverse phase liquid chromatography;
RSD: Relative standard deviation;
SBSE: Stir-bar sorptive extraction;
SDB-RPS: Sulfonated styrenedivinylbenzene;
SDME: Single drop microextraction;
SFE: Supercritical fluid extraction;
SIM: Selected Ion monitoring;
SPE: Solid phase extraction;
SPME: Solid phase microextraction;
TBT: Tributyltin;
TCMTB: 2-(thiocyanatomethyl thio) benzothiazole;
TMPAH: Trimethylanilinium hydroxide;
TPBP: Triphenylborane pyridine;
TPT: Triphenyltin;
UHPLC: Ultra-high performance liquid chromatography.

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