Cent. Eur. J. Chem. • 10(3) • 2012 • 521-533
DOI: 10.2478/s11532-011-0154-z

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Central European Journal of **Chemistry**

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

Review Article

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Received 26 September 2011; Accepted 27 November 2011

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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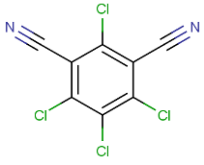
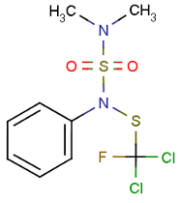
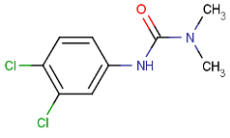
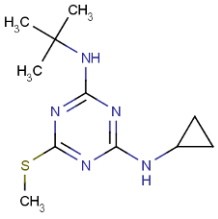
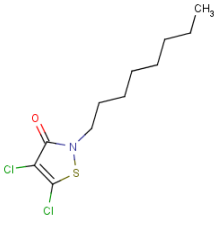
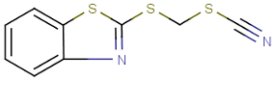
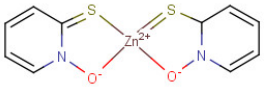
Table 1. Common booster biocides found in antifouling paints.

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].