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Original scientific paper

Determination of cybutryne content in antifouling paint using amperometry based on the specific electrochemical oxidation reaction

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Abstract

Cybutryne is widely used as an antifouling biocide and is one of the chemicals most frequently detected in the marine ecosystem. However, its use is restricted due to its significant adverse effects on the marine environment. In this paper, we report a simple amperometric method for determining cybutryne content in antifouling paints, utilizing the electrochemical oxidation of cybutryne in an anhydrous acetonitrile medium. Current measurements were performed by applying a potential of +2.0 V vs. SCE in 0.1 M NaClO₄-CH₃CN solution. The results showed a linear increase in current corresponding to cybutryne concentrations in the range of 10 to 700 mg L⁻¹, with a detection limit of 3.82 mg L⁻¹. An excellent linear relationship was observed between the concentration of cybutryne extracted from antifouling paints and the amperometric response. The correlation coefficient exceeded 0.99, recoveries ranged from 89.5 to 102.0 %, and the relative standard deviation was less than 4 %. Analysis of real samples confirmed that this electrochemical method meets the requirements for cybutryne detection in antifouling paints, offering high selectivity, rapid analysis, high sensitivity, and good reproducibility.

Keywords

Protective paint; marine environment; phytotoxic biocide; amperometric detection, antifouling interfering agents

Introduction

Antifouling paints are widely used in maritime transport and marine-related industries because they effectively prevent damage caused by the attachment of marine fouling organisms. However, the biocides contained in these paints not only eliminate fouling organisms but also adversely affect non-target marine life. This threatens the stability of the marine food chains, disrupts the balance of the marine ecosystem, and ultimately poses a risk to human health [1-3]. Tributyltin (TBT), once widely used as an antifouling biocide, was banned internationally in 2008 due to its toxicity to non-target organisms [4]. Subsequently, the antifouling paint market shifted toward using copper compounds and booster biocides, which have lower emission rates [5,6].

Among the various antifouling biocides, cybutryne (2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine) has been widely used due to its high efficacy in inhibiting growth by disrupting electron transport within the photosynthetic systems of marine and freshwater algae [7-9]. However, this compound leaches into seawater and can negatively impact the growth of non-target photosynthetic organisms, such as marine phytoplankton, periphyton, aquatic plants and corals [10,11]. Furthermore, it is resistant to biodegradation and has a half-life generally exceeding 100 days, resulting in a greater negative impact on the marine environment compared to other antifouling biocides. As this compound is known to be a hazardous substance that causes pollution in marine ecosystems, the International Maritime Organization (IMO) decided to restrict the use of cybutryne starting in 2023.

Most analytical methods for the quantification of cybutryne are based on gas chromatography (GC) or liquid chromatography (LC) techniques capable of achieving very low detection limits [12-16]. However, these techniques are unsuitable for the routine monitoring of cybutryne in antifouling paints, as they not only require expensive equipment but also necessitate time-consuming sample pretreatment processes, such as solid-phase extraction (SPE) or micro-SPE [17,18].

Electrochemical analysis methods are widely used as alternatives to chromatographic techniques because they are not only simple and rapid but also offer excellent detection performance. Immunosensors incorporating antibody-modified self-assembled monolayers (SAMs) are frequently chosen as powerful analytical tools for *in-situ* detection of cybutryne using amperometry or voltammetry [19-22]. These immunosensors rely on antibody-antigen interactions, utilizing antibodies specific to the target antigen as capture agents. Such capture molecules are immobilized on the sensor surface or substrate, converting the specific antibody-antigen binding reaction into a measurable physical signal. The detection limit of the immunosensor and the intensity of the converted signal depend on the efficiency of the antibody-antigen binding [23]. Additionally, a method for rapid *in-situ* potentiometric measurement has been reported using a cybutryne-selective microelectrode that employs a novel ion-pair complex, $[\text{Irgarol-H}]^+[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$, as the active site for selective recognition [24]. This cybutryne-selective microsensor demonstrated high selectivity for cybutryne compared to other potentially interfering co-biocides. While other methods, such as those utilizing Raman spectroscopy [25], exist, biosensors and selective electrodes often require complex fabrication processes and expensive reagents, and their practical applications remain limited. Therefore, there is a need to develop more cost-effective and rapid electrochemical analysis techniques for detecting biocides like cybutryne in antifouling paints.

Cybutryne generally exhibits electrochemical activity at $\text{pH} < 7$ [26,27], and most electrochemical analyses of this compound to date have been based on electrochemical reduction reactions under low-pH conditions. Since other co-biocides with similar properties also display comparable electrochemical reduction behaviour [23,28], selective electrodes are required to distinguish between

them. Cybutryne belongs to the class of s-triazine herbicides, which are highly resistant to oxidation. While the oxidation reactions of other co-biocides widely used in antifouling paints (*e.g.* diuron, a phenylurea) typically occur in the 500 to 1300 mV range [29-32], the oxidation signals of thi-omethylated s-triazine derivatives, including cybutryne, appear in the 1700 to 2000 mV range [33]. Due to the characteristics of these anodic oxidation signals, it was confirmed that the compound could be easily detected via these signals in a polar aprotic solvent with a wide electrochemical window, without the need for selective electrodes.

Therefore, this study reports a rapid electrochemical analysis method for the simple and cost-effective detection of cybutryne in antifouling paints.

Experimental

Materials

Cybutryne (99.0 % purity), diuron (98.5 % purity), benzofluorosulfamide (99.0 % purity), anti-fouling biocide Sea-Nine 211 (98.0 % purity), ethyl acetate (analytical grade), and acetonitrile (analytical grade) were purchased from Sigma-Aldrich (Shanghai, China). Sodium perchlorate (NaClO_4 , analytical grade) was purchased from Aladdin Biochemical Technology Co., Ltd. A stock standard solution of cybutryne was prepared by dissolving the compound in anhydrous acetonitrile containing 0.1 M sodium perchlorate (0.1 M $\text{NaClO}_4\text{-CH}_3\text{CN}$). The platinum plate working electrode, platinum wire counter electrode, and saturated calomel reference electrode (SCE) were purchased from Shanghai Chenhua Instrument Co., Ltd.

Sample extraction and preparation

About 0.5 g (± 0.0001 g) of the paint sample was taken, placed into a 10 mL stoppered test tube, adjusted to a mark with ethyl acetate, mixed with a vortex mixer (MX-S, DLAB Scientific Co., Ltd., Beijing, China), ultrasonically extracted for 10 min using an ultrasonic bath (KQ-250DB, Kunshan Ultrasonic Instruments Co., Ltd., China), and the supernatant was filtered through a 0.22 μm organic PTFE filter membrane (Tianjin Jinteng Experiment Equipment Co., Ltd., China). The resulting solution was transferred to a beaker and thoroughly dried at 80 °C overnight in a laboratory oven (DHG-9030A, Shanghai Jing Hong Laboratory Instrument Co., Ltd., China). The dried sample was again placed in a 10 mL stoppered tube and redissolved in anhydrous acetonitrile containing 0.1 M sodium perchlorate using an ultrasonic bath. When the concentration of the measured compounds is too high, the sample was appropriately diluted before use.

Electrochemical measurements

Cyclic voltammetry (CV) and amperometric measurements were performed using a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). A three-electrode system was employed, consisting of a platinum plate (surface area: 2.0 cm^2 , dimensions: 10×10 mm) working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) reference electrode. CVs were recorded at room temperature in a 0.1 M $\text{NaClO}_4\text{-CH}_3\text{CN}$ electrolyte solution containing 0.01 M cybutryne. The potential range for electrochemical measurements was set to ± 2.5 V, with scan rates of 100 and 1000 mV s^{-1} applied. CV measurements were conducted starting from 1.2 V in the positive direction. Amperometric measurements were carried out by successively adding required amounts of cybutryne to the 0.1 M $\text{NaClO}_4\text{-CH}_3\text{CN}$ electrolyte solution. The applied potential was set to 2.0 V (*vs.* SCE), a value slightly higher than the peak potential

identified in the CV study. Analytical performance was evaluated based on parameters such as linearity, limit of detection (LOD), reproducibility, and selectivity.

Results and discussion

Sample extraction

A custom sampling device was used to extract biocide samples from antifouling paint, thereby preventing damage to the protective surface coating and minimizing the inclusion of the underlying anti-corrosive layer during the sampling process. The extraction solvent needed to exhibit high solubility for the analytes without interfering with the analysis. Previous studies [30] confirmed that ethyl acetate meets these requirements and offers relatively high extraction efficiency. Extraction with ethyl acetate dissolved only organic antifouling agents; other antifouling agents, such as copper and zinc complexes, were not extracted. Therefore, ethyl acetate was selected as the extraction solvent. For the electrochemical oxidation of cybutryne, the dried sample was redissolved in anhydrous acetonitrile.

Electrochemical measurements of cybutryne

The electrochemical oxidation of cybutryne, a thiomethylated s-triazine derivative, occurs *via* the exocyclic aliphatic amino groups at the 4- and 6-positions. Figure 1 shows the CV curves of 0.1 M $\text{NaClO}_4\text{-CH}_3\text{CN}$ solution containing 250 mg L^{-1} of dissolved cybutryne at different scan rates. In nonprotonic polar anhydrous media, no hydrolytic or other interfering effects are observed, facilitating the isolation and identification of the test substance. Cybutryne belongs to the s-triazine class of herbicides, a group of compounds characterized by high resistance to oxidation. Therefore, electrochemical studies using anhydrous acetonitrile were conducted to investigate the electrochemical oxidation of this substance. As shown in Figure 1, a slight anodic current begins to appear near a scan potential of 1.6 V, and a distinct oxidation current peak is observed at 1.96 V as the potential shifts in the positive direction. This oxidation peak is attributed to the electrochemical oxidation of cybutryne. Furthermore, as the scan rate increased from 100 to 1000 mV s^{-1} , the oxidation signal of cybutryne was effectively amplified, resulting in a significant increase in the oxidation peak current from approximately $1.75 \text{ }\mu\text{A}$ to $5.2 \text{ }\mu\text{A}$. This marked increase in peak current suggests that the electrochemical oxidation of cybutryne is a diffusion-controlled process. The absence of a corresponding reduction peak during the reverse scan in the CV measurements confirms the irreversibility of the oxidation reaction.

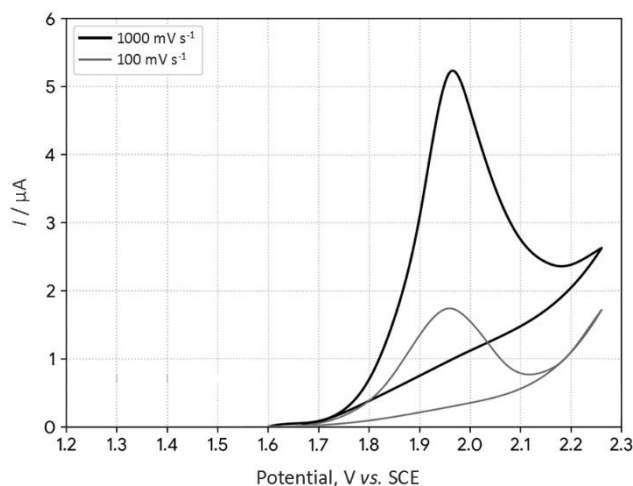


Figure 1. CV curves of 250mg/L cybutryne dissolved in 0.1M $\text{NaClO}_4\text{-CH}_3\text{CN}$ solution at different scan rates

In general, the electrochemical oxidation of aliphatic amines universally initiates with a rate-determining, single-electron transfer from the nitrogen lone pair to the electrode surface. At an applied potential of 1.96 V, this initial loss of an electron generates a highly reactive and unstable ammonium radical cation intermediate. In an anhydrous acetonitrile medium devoid of proton donors, this radical cation undergoes rapid stabilization *via* α -deprotonation or radical decomposition pathways. These swift subsequent chemical reactions effectively shift the equilibrium and prevent the reverse reduction process, thereby fully accounting for the completely irreversible nature observed in the CV. This electrochemical oxidation mechanism aligns with the classical mechanism commonly observed for sterically hindered secondary aliphatic amines [34].

Amperometric analysis of cybutryne was performed in a 0.1 M NaClO₄-CH₃CN electrolyte solution using an applied potential of 2.0 V vs. SCE (Figure 2). Generally, current response is limited by slow reaction kinetics at low potentials, whereas background noise increases significantly at high potentials due to the onset of electrolyte decomposition. Based on the CV analysis, 2.0 V a potential slightly higher than the oxidation peak potential, was selected as the applied potential for amperometric detection. An applied potential of 2.0 V appears capable of successfully achieving the maximum steady-state oxidation current while maintaining low background noise and a rapid stabilization time. As shown in Figure 2, distinct dynamic current responses were observed upon the addition of cybutryne at various concentrations. The current increased clearly, stably, and rapidly in a stepwise manner. An instantaneous rise in current occurred immediately upon the addition of cybutryne, and a steady state was reached within 3 seconds.

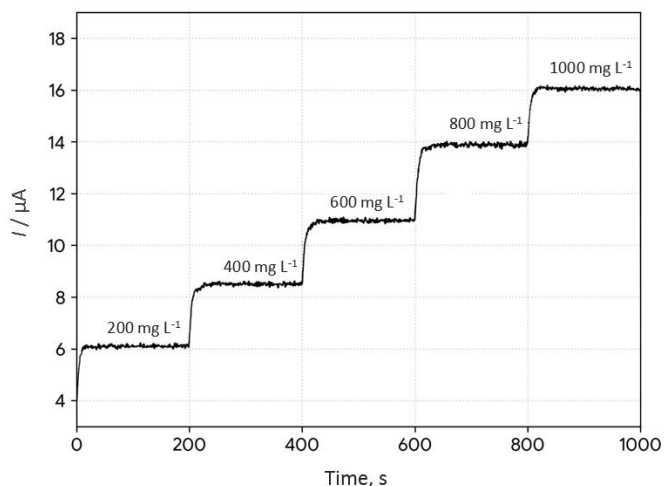


Figure 2. *I-t* curve for successive addition of 100 mg L⁻¹ of cybutryne in electrolyte of 0.1 M NaClO₄-CH₃CN

Sensing performance for cybutryne

A calibration curve for the detection of cybutryne was constructed in the concentration range of 10 to 700 mg L⁻¹ using 0.1 M NaClO₄-CH₃CN as the electrolyte. The standard calibration curve, linear relationship, and correlation coefficient are shown in Figure 3a. Analysis of standard solutions at various concentrations using the amperometric method revealed a good linear relationship between current and concentration. Based on a signal-to-noise ratio of 3:1, the limit of detection (LOD) for cybutryne was determined to be 3.82 mg L⁻¹. This level is below the maximum permissible usage limit for cybutryne. These experimental results indicate that the amperometric method is applicable to the analysis of cybutryne in target samples.

Reproducibility was evaluated by performing seven consecutive measurements using a 0.1 M NaClO₄-CH₃CN solution containing 400 mg L⁻¹ of cybutryne.

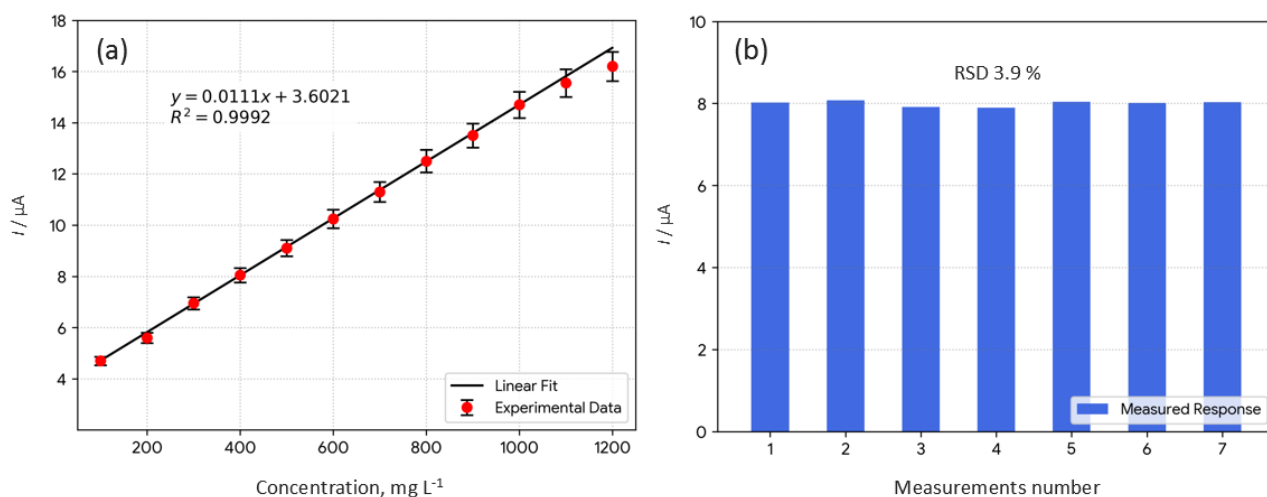


Figure 3. a) Standard linear curve of cybutryne at amperometric analysis, b) current response of 400 mg/L cybutryne in 0.1 M NaClO₄-CH₃CN solution in seven consecutive measurements

As shown in Figure 3b, the relative standard deviation (RSD) for the seven consecutive measurements was less than 4 %. Subsequently, recovery experiments using the standard addition method were conducted with acrylic resin paint (A) and epoxy paint (B) as matrix samples. Cybutryne standard solutions at various concentrations (10, 100 and 500 mg kg⁻¹) were added to each matrix solution, followed by analysis using the established electrochemical method. All measurements were performed in triplicate. The resulting recovery and precision data are presented in Table 1. The results demonstrated RSDs of less than 4 % and recoveries ranging from 89.5 to 102.0 % for cybutryne across all concentration levels. This confirms that the proposed method possesses high accuracy and excellent precision for the determination of cybutryne in real paint matrices.

Table 1. Recovery and precision of cybutryne determination in acrylic resin (A) and epoxy (B) paint matrices

Sample	Concentration, mg kg ⁻¹			Average recovery, %	RSD, %
	Nominal	Measured	Mean		
A	10	10.71, 10.47, 9.87, 10.24, 10.03, 9.89	10.02	102.0	3.31
	100	91.65, 92.46, 91.34, 90.13, 90.97, 89.68	91.12	91.1	1.17
	500	455.48, 453.08, 448.75, 448.95, 438.00, 441.92	447.70	89.5	1.48
B	10	9.51, 9.73, 9.65, 9.59, 9.56, 9.34	9.56	95.6	1.41
	100	93.39, 93.61, 95.69, 91.87, 92.13, 92.52	93.20	93.2	1.50
	500	453.30, 450.76, 458.42, 441.97, 450.54, 441.38	449.40	89.9	1.47

Selectivity

To evaluate selectivity, three representative antifouling agents (diuron, benzylfluorosulfamide, and Sea-Nine 211), which can be selectively extracted in ethyl acetate solvent with cybutryne, were used as interfering species. Amperometric measurements were conducted in an electrochemical cell using solutions containing these interfering substances at concentrations ranging from 5 to 100 mg L⁻¹. The selectivity coefficients derived from these measurements are shown in Figure 4. As shown in Figure 4, only Sea-Nine 211 caused slight interference with cybutryne detection, while the impact of the other substances was negligible. This is because the anodic waveforms for all the interfering substances appear at potentials below 1300 mV. Since the amperometric analysis based on anodic waveforms is largely unaffected by the presence of these interfering substances commonly found in antifouling paints, it demonstrates high selectivity for cybutryne.

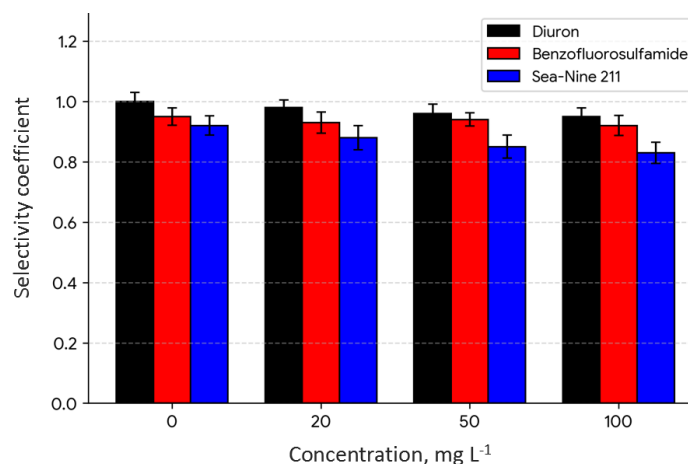


Figure 4. Selectivity of cybutryne determination for three interfering species (diuron, benzofluorosulfamide, Sea-Nine 211)

Table 2 summarizes the comparative performance of various analytical methods for determining cybutryne content. While most existing methods offer excellent sensitivity and low limits of detection, they suffer from drawbacks regarding equipment costs, processing speeds, and procedural complexity. The oxidation-based amperometric method proposed in this paper effectively overcomes these limitations by utilizing cybutryne's characteristic high-potential anodic wave. This anodic wave targets a specific irreversible oxidation peak of cybutryne at 1.96 V. Because common interfering paint biocides (such as diuron) possess oxidation waves well below this window at 500 to 1300 mV, this method achieves exceptional matrix selectivity using a bare platinum electrode layout without tedious chemical modification. Furthermore, while the detection limit (3.82 mg L⁻¹) is relatively high compared to other high-sensitivity sensors, it remains well below the maximum regulatory limits for paint applications. With a broad linear dynamic range (10 to 700 mg L⁻¹) and a rapid response time (approximately 3 seconds), this technology offers an optimized balance of speed and cost-effectiveness for monitoring antifouling paints in real-world environments.

Table 2. Comparison of different analytical methods for the determination of cybutryne

Analytical technique	Target matrix	Linear range	LOD	Main characteristics	Ref.
LC-ESI-MS/ IL-DLLME	Seawater/ lake water	0.5 to 200 µg L ⁻¹	0.01 to 0.1 µg L ⁻¹	- High selectivity - High enrichment factor - Slow turnaround	[15]
CapLC	Environmental water	Low ng L ⁻¹ range	Trace level	- Automated micro-extraction - Eco-friendly configuration - Poor response velocity	[16]
BiMW interferometer	Undiluted seawater	Low ng L ⁻¹ range	3 ng L ⁻¹	- Ultra-high sensitivity - Direct kinetics monitoring - Complex surface modification	[21]
Potentiometric microsensor	Seawater / aquatic environment	1 to 1000 µM	2 µM	- Fast response time - High portability - Complex electrode modification	[24]
Amperometry	Antifouling paint	10 to 700 mg L ⁻¹	3.82 mg L ⁻¹	- High selectivity - Simple sample preparation - Industrial target matrix	This study

LC-ESI-MS: liquid chromatography - electrospray ionization - mass spectrometry; IL-DLLME: ionic liquid - dispersive liquid- liquid microextraction; CapLC: capillary liquid chromatography; BiMW: bimodal waveguide

Actual sample detection

Analysis of the collected marine antifouling paints using this method revealed that the cybutryne content agreed with the actual content. The results indicate that the analytical method established

in this study effectively separates cybutryne from the samples and offers excellent reproducibility and analysis speed, making it suitable for measuring cybutryne in marine antifouling paints.

Conclusions

In this study, we proposed an amperometric method based on the electrochemical oxidation of cybutryne as a simple technique for detecting this harmful component found in marine antifouling paints. Analytical samples were prepared by extracting the target substance with ethyl acetate, drying the extract, and redissolving it in anhydrous acetonitrile. Cybutryne exhibited a selective electrochemical reaction showing the oxidation peak potential of approximately +1.96 V vs. SCE. An excellent linear relationship was confirmed between the measured charge and the cybutryne concentration (correlation coefficient >0.99, limit of detection: 3.82 mg L⁻¹). Recoveries ranged from 89.5 to 102.0 %, and the RSD was less than 4 %. Experiments with real-world samples demonstrated that this method offers excellent selectivity, speed, sensitivity, and reproducibility. This simple electrochemical analysis technique provides a robust technical foundation for the routine monitoring of marine paints.

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