DETERMINATION OF ZN- PYRITHIONE IN ADRIATIC COASTAL SEAWATER SAMPLES BY CATHODIC STRIPPING VOLTAMMETRY

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Abstract

A method was adapted here to determine the anti-foulant pyrithione in natural waters. The method is based on cathodic stripping voltammetry (CSV) in the presence of Triton-X-100 to separate the pyrithione peak from interfering thiol compounds. The detection limit in UV-digested seawater was 1.5 nM for a deposition time of 60s. The method is applied for the determination of Zn- pyrithione in coastal samples of the Adriatic sea.

Key words: Zn-pyrithione, electrochemistry, Adriatic sea, anti-foulant

Introduction

Zinc pyrithione, ZPT, (zinc-2-pyridinethiol-N-oxide (IUPAC), CAS [13463-41-7]), belongs to a group of antifouling paint booster biocides which are added to antifouling paints to improve their efficacy. These biocides have become prevalent , followed a ban on the use of triorganotin biocides in antifouling paints for small boats in the late 1980's[1]. ZPT is used extensively also an antiseborrehic agent in hair care [2]. Both of these commercial applications made ZPT an analyte of interest . Several studies of the fate of pyrithione in the environment and its toxicity to aquatic life have been made [2,3]. Goka [2] showed on Zebrafish and Japanese Medaka that ZPT induces significant teretogenic effects on larvae of both species. Kobayashi and Okamura [3] found ZPT much more toxic to sea urchins than tributyltin oxide (TBTO). Assessment of the impact of pyrithiones (PT) has been complicated by lack of a sensitive and reproducible method of analysis. Methods developed for detection of ZPT in hair care and cosmetic products (HPLC and polarography) [4,5] could in principle be used for natural waters but they require a very large preconcentration step suffering from poor recovery and reproducibility. The method developed recently [6], for analytical determination of ZPT in natural waters in the presence of Triton-X-100, has good reproducibility, sensitivity and can alleviate the influence of other S - containing compounds which are present in natural waters. This newly developed method is applied here for the determination of ZPT in samples from the coastal area of the Adriatic sea, Mersey river estuary and marinas.

Experimental

Instrumentation and reagents

The voltammetric system comprised a μAutolab voltammeter (Ecochemie) and a static mercury drop electrode (Metrohm 663VA), PC-controlled using GPES 4.8 Windows software (Ecochemie). The reference electrode was double junction Ag/saturated AgCl with a salt bridge filled with 3M KCl. The counter electrode was a glassy carbon rod, and the voltammetric cell was glass. A 1 mM stock solution of zinc pyrithione (SIGMA) was prepared weekly. A potential of -0.1 V was applied to adsorb the pyrithione using an adsorption time of typically 60 s. Then an equilibration time of 10 s was allowed, and the potential was scanned in the differential-pulse mode from -0.05 to -1.2 V. (modulation time 0.01 s, interval 0.1 s, step height 0.010 V and pulse amplitude 0.050 V).

Results and discussion

Pyrithione gives a peak at -0.3 V in the presence of Triton-X-100 (2-4ppm), when added to pH 9 (ammonia buffer) seawater sample. Cyclic voltammetry (CV) across a long potential range (-0.05V to -1.2V) showed that the voltammetric peaks for ZPT and glutathione are well separated , even in the presence of 1000nM of glutathione. The first peak appears at a potential E = -0.3 V and is due to the reduction of mercury in an adsorbed complex with pyrithione, while the second peak appears at E = -0.5 V and is due to the presence of glutathione in the sample .

The height and potential of the ZPT peak are affected by variations in the pH and electrochemical parameters (adsorption time, potential, etc), and by the concentration of Triton-X-100 which is used for much improved sensitivity.

It has been reported that low water solubility and rapid photodegradation are probably significant factors in the removal of ZPT from surface waters, with a half-life of 4 hours under ambient room light [7]. The pyrithione is indeed readily broken down by ambient UV light, but it is likely that such UV is much reduced in estuarine waters , marinas and in waste water outfalls, so it is not known whether the photolytic process is important in nature. Samples stored under ambient conditions appeared stable. After 8 hours standing under ambient conditions in a translucent polyethylene bottle on the lab bench, the remains of the bulk solution containing 200 nM of ZPT were analysed and produced peaks of equal height to the original measurements made with fresh sample[6]. Localized high concentrations of pyrithione could be expected due to the reduced UV light , embayment of high concentration waters in marinas or at waste water outfalls.

The marina sample (within a docks complex off the River Mersey ; UK) was determined to contain 105 ± 5 nM pyrithione [6]. A sample from the marine Rogoznica lake (Croatia, in the vicinity of marina Frapa) was found to contain 120 ± 5 nM pyrithione. Seawater samples from other coastal areas of the north Adriatic sea were analysed as well. The concentrations in these samples were 24-44 nM of pyrithione.

Conclusion

These preliminary measurements indicate that pyrithione may well occur widespread in the environment, and it will be interesting to investigate its source and fate (anti-fouling agent, shampoos, or other) in different coastal waters.

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