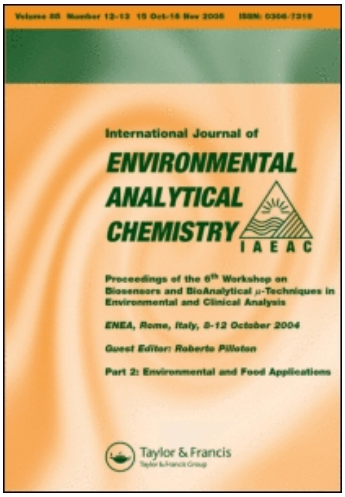

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Direct analysis of zinc pyrithione using LC-MS

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Zinc pyrithione has been widely used as one of the booster biocides in antifouling paints on the bottom of vessels. A direct analysis method for zinc pyrithione has been developed using LC-MS without trans-chelation and degradation. The addition of ammonium acetate in mobile water phase was effective in stabilizing zinc pyrithione in HPLC, and the optimal concentration was 20 mM. The lower temperature was favourable in preventing decomposition and transformation. The column temperature was set at 298 K. The temperatures of the drying gas and the vaporizer in the mass-selective detector were found to be 523 K. Under these conditions, a mass spectrum and chromatogram of zinc pyrithione in methanol were successfully obtained by LC-MS for concentrations between 3.5 and 10 mg L^{-1}.

Keywords: Zinc pyrithione; HPLC-MS; Anti-fouling paint; Booster biocide

1. Introduction

Fouling of ships' hulls has been a serious problem, resulting in an increase in fuel consumption and frequent dry docking. The history of ships and seamen struggling with fouling organisms on ships' hulls goes as far back as ancient Mediterranean times. A variety of materials, such as tar, wax, copper plating, arsenic, and mercury compounds have been used. Organotin compounds (OTCs), such as tributyltin (TBT) and triphenyltin (TPT), were found in the 1960s to have outstanding antifouling properties. However, it was found that leaching of such compounds from ships' hulls has severe environmental side effects on non-target organisms, and coastal environments are damaged by the use of OTCs in worldwide. Many countries have banned the use of OTCs in antifouling paints for most ships since the late 1980s, and the International Maritime Organization agreed to phase out the use of OTC antifouling paints on

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ships by 2003. As a result, a wide variety of booster biocides have been introduced as a substitute for OTCs [1, 2].

One of the major booster biocides in anti-fouling paints is zinc pyrithione, bis(1-hydroxy-2(H)-pyridethionato-*O*,*S*)-T-4 zinc (ZnPT), which has been widely used as a bactericide, fungicide, algicide, and even an antidandruff agent.

ZnPT has been reported to be very toxic to marine organisms [3] and to degrade rapidly in the aquatic environment [4, 5]. For an environmental-risk assessment or environmental-fate analysis of ZnPT, its direct analysis is essential, so as to distinguish ZnPT from other pyrothione compounds. In most of the previous studies [6–8], ZnPT was converted to copper pyrithione and analysed as described later in this section. ZnPT should be analysed by itself directly, because the toxicity of the pyrithione compounds is dependent on the chelating ions. The direct analysis of ZnPT is desirable not only for monitoring environmental concentration but also for inspecting a ship's hull paint, laboratory experiments for leaching, and degradation rates.

An analytical method of ZnPT concentration has been developed using chelate exchange [6], polarography [9], thin-layer choromatography [10], and HPLC [7, 8, 11–14]. LC analysis of ZnPT has required special procedures, such as pre-labelling with *N*-dansylaridine [12], intentional *trans*-chelating to copper pyrithione [7, 8], use of a metal-free system for LC [13], or use of a polymer column [14]. Although only LC is applicable to determine of ZnPT, the direct analysis has not been well established due to its interactions with materials in the LC system.

In this study, a direct analysis method of ZnPT has been developed using LC-MS, suppressing its thermal decomposition and transchelation.

2. Experimental

2.1. *Materials and sample preparation*

Methanol of PCB analysis grade was obtained from Junsei Chemical Co. Ltd (Tokyo). Trifluoroacetatic acid (98%), ammonium acetate solution (10 mol L^{-1}, for genetic engineering), ammonium thiocyanate solution (0.1 mol L^{-1}, for volumetric analysis), and zinc pyrithione (90%) were obtained from Wako Pure Chemical Industry Ltd (Tokyo). Ultrapure water was produced using a Millipore Milli-Q water purification system. Zinc pyrithione standard solutions were made up to 1.0, 3.5, 5.0, and 10.0 mg L^{-1} in methanol.

2.2. *LC and mass spectrometry*

LC was carried out using an Agilent 1100 series fitted with a quaternary pump, analytical columns with temperature control system, and a diode array detector. Unison UK-Phenyl columns (2.0×50 mm or 3.0×50 mm) supplied by Imtakt Co. (Kyoto, Japan) were used, considering weak interactions between zinc pyrithione and phenyl column compared with ODS columns. The mobile phase was a methanol–water solution, and trifluoroacetatic acid, ammonium, thiocyanide, and ammonium acetate were tested as buffer agents in the mobile water phase. A non-metallic flit was applied to avoid any contact with metals in the LC.

Mass spectra were obtained using the Agilent 1100 series quadrupole mass-selective detector. The analysis was carried out in APCI positive ion mode. Single ion monitoring (SIM) was performed at m/z 316.9 $[M+H]^+$ as zinc pyrithione.

2.3. *Thermogravimetric analysis*

Thermogravimetric analysis of solid zinc pyrithione was carried out at a heating rate of $10\,K\,min^{-1}$ from room temperature to 800 K using an Ulvac TGD-9600 fitted with thermogravimeter/differential scanning calorimeter and differential thermal analyzer.

3. Results and discussion

3.1. *Effect of operating parameters of LC-MS*

Zinc pyrithione reacts with other metal cations and is degradable at high temperatures. For the direct analysis of ZnPT, it is essential to stabilize ZnPT in LC and MS. The operating conditions of LC and MS were optimized to prevent thermal and chemical decomposition, based on the parametric investigation on the composition of the mobile phase and the temperatures in the apparatus.

3.1.1. Conditions of LC

1. *Effect of buffer solutions in mobile water phase*: Zinc pyrithione is chemically unstable and reacts readily with other metallic cations. This transchelation may take place even in LC and causes difficulties in the analysis. Therefore, the buffer agent (trifluoroacetatic acid, ammonium thiocyanide, or ammonium acetate) was added in the mobile water phase to stabilize zinc pyrithione in LC. The chromatographic peak of zinc pyrithione, which was detected by the diode array, was obtained only for ammonium acetate. Ammonium acetate is considered to be effective in decreasing activities of metallic ions, mainly copper. The ammonium ion forms a stable complex with Cu(II) ion. The Cu^{2+} cation dose not attack zinc pyrithione because the $[Cu(NH_3)_4]^{2+}$ complex may be formed from the Cu^{2+} cation and NH_3 ion. The relationship between the concentration of ammonium acetate in the mobile water phase and peak intensities was investigated. The concentration of ammonium acetate was 0–40 $mg\,L^{-1}$. The result is shown in figure 1. The maximum intensity of the zinc pyrithione peaks was obtained with 20 mM ammonium acetate in the mobile water phase. The peak did not appear when the mobile phase was water only. The addition of ammonium acetate would help to maintain the appropriate pH to stabilize of zinc pyrithione.
2. *Effects of column temperature*: The effect of the column temperature was also investigated. The chromatograms were detected and compared by the diode array obtained at the column temperatures at 293 and 313 K. The peak of 293 K was sharper, and its retention time was longer than that of 313 K, suggesting that the transchelation rate in the column could be reduced by lowering the temperature.

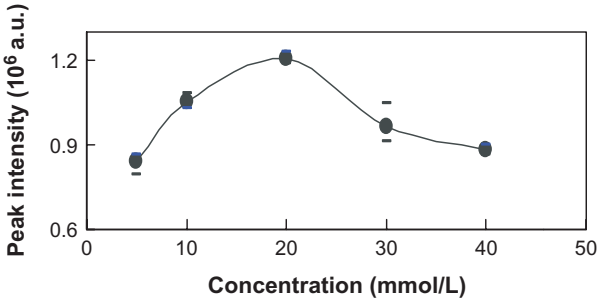

Figure 1. Effect of ammonium acetate concentrations on the zinc pyrithione peak area measurement by LC/MS.

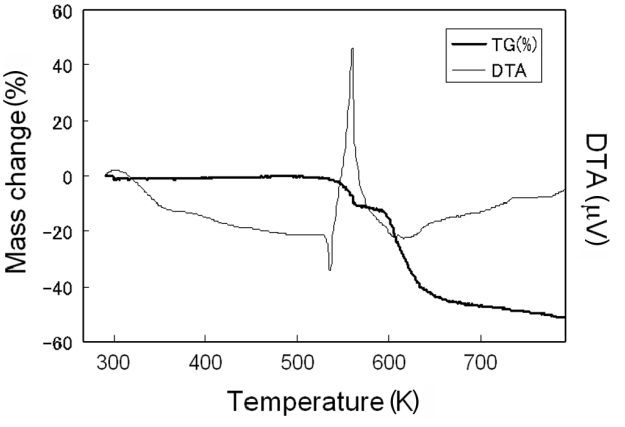

Figure 2. Thermogravimetric spectrum of zinc pyrithione.

3.1.2. Mass-detector conditions

1. *Thermogravimetry*: Pyrolysis of zinc pyrithione at high temperatures causes another difficulty in MS analysis. The thermogravimetry of zinc pyrithione in air, shown in figure 2, reveals that the thermal degradation of zinc pyrithione starts at about 520 K. This suggests that zinc pyrithone may decompose in a mass-selective detector, and the temperature of the nebulizer and drying gas should not be too high.
2. *Temperature of flow gas and nebulizer in mass selective detector*: The effect of the temperature of the flow gas and vaporizer on the mass intensity at m/z 316.9 was investigated when the flow gas temperature was between 423 and 573 K, and the vaporizer temperature was between 473 and 573 K. The peak at m/z 316.9 corresponds to the addition of proton to zinc pyrithione $[M + H]^+$; the relationship between the mass intensities on the vaporizer and the flow gas temperatures is shown in figure 3. The maximum intensity was obtained when both vaporizer and flow gas temperatures were 523 K, respectively.

3.2. *Chromatogram and mass spectra*

Based on the above discussion, the optimal operating parameters of LC-MS for ZnPT analysis were determined and are listed in table 1. A chromatogram and mass spectra

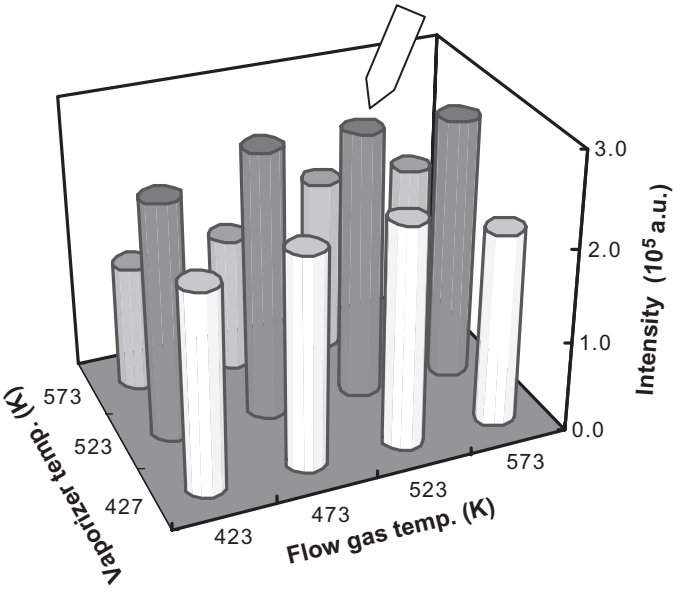

Figure 3. Relationship between mass intensity and temperature of the flow gas and nebulizer in the mass-selective detector.

Table 1. Optimal conditions for zinc pyrithione using LC/MS.

LC
Instrument: Agilent 1100
Mobile phase
A = 20 mM ammonium acetate H_2O
B = MeOH
A : B = 50 : 50
Flow rate: 0.5 mL min^{-1}
Injection: 3 μL
Column: Unison UK-Phenyl 50 × 3 mm
Temperature of column: 293 K
MS
Instrument: Agilent 1100MSD SL
Ionization: APCI positive mode
Nebulizer pressure: 60 psig
Flow gas: N_2
Flow rate: 4 L min^{-1}
Temperature: 523 K
Scan (m/z): 100 ~ 500
V_{cap}: 2500 V
Corona current: 4 mA
Vaporizer temperature: 523 K
Fragment voltage: 100 V

of ZnPT methanol solution were obtained, as shown in figure 4. The main peak at m/z 316.9 corresponds to the addition of proton to ZnPT $[M+H]^+$, and the peaks at m/z 318.9 and 320.9 correspond to those including isotopic zinc. The fragment of m/z 128 is attributed to the pyrithione ligand. The calibration curve was found to show a good linearity, as shown in figure 5 in a range of concentrations between 3.5 and 10 mg L^{-1} with a correlation coefficient of 0.996. An equation of $y = 6767x - 22\,041$

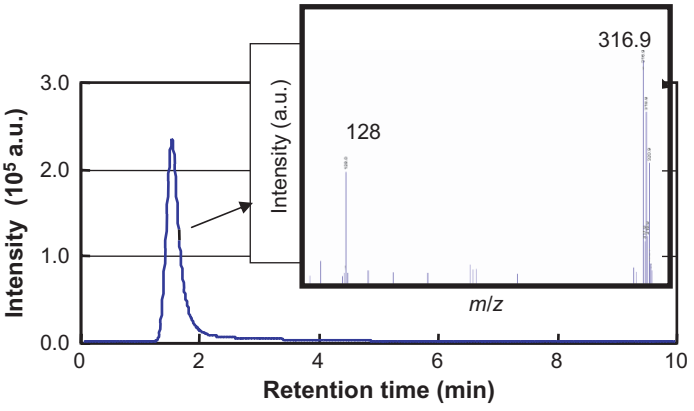

Figure 4. LC/MS chromatogram and MS spectra of 10 mg L^{-1} of zinc pyrithione.

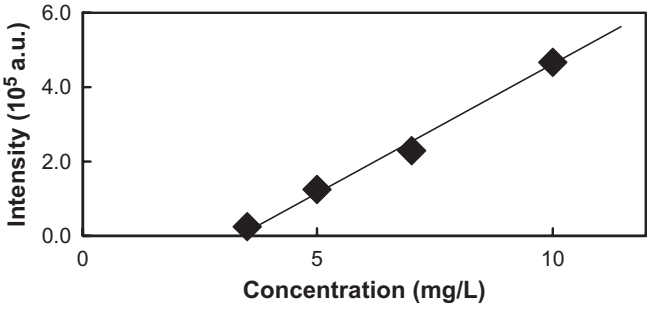

Figure 5. Calibration curve of zinc pyrithione.

was formulated, with a correlation coefficient of 0.996. Repeated injections ($n = 5$) 3.5 mg L^{-1} demonstrated that the method also yields a good precision (average intensity: 262.4; the standard deviation: 6.7). However, the detection limit is still too high to use for environmental monitoring. The peak was broken down when the concentration was below 3.5 mg L^{-1}. An increase in the amount of sample injected would improve the detection limit but would also reduce the sharpness of the peak and linearity of the calibration curve. Further optimization of LC-MS conditions could be investigated in the future. For example, by using electro-spray ionization, the mass intensity would be stronger than that which would be obtained using atmospheric pressure ionization.

4. Conclusions

A direct analysis of zinc pyrithione was successfully carried out using LC-MS by suppressing the transchelation and pyrolysis of zinc pyrithione. Although further improvements in detection limit are needed, the proposed method clearly shows a possibility of monitoring the environmental concentration and evaluating the environmental risk.

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References

[1] Report of Japan Paint Manufacturers' Association. Self-Regulatory Management of Japan Print Manufacturers' Association to comply with IMOs. International Convention on the Control of Harmful Anti-Fouling System on Ships, 2001, pp. 1–38. Available online at: http://www.toryo.or.jp/jp/anzen/index.html (accessed 2005).
[2] Pesticide Safety Directorate and Health and Safty Executive. *Pesticides 2000*, pp. 337–388, The Stationery Office, Norwich, UK (2000).
[3] N. Kobayashi, H. Okamura. *Mar. Pollut. Bull.*, **44**, 748 (2002).
[4] P.A. Turley, R.J. Fenn, C. Ritter. *Biofouling*, **15**, 175 (2000).
[5] Y. Yamaguchi, A. Kumakura, M. Ishigami, K. Shibata T. Senda, Y. Yamada. Paper presented at *Proceedings of International Symposium on Antifouling Paint and Marine Environment*, p. 228 (2004).
[6] B.L. Kobacoff, C.M. Fairchild. *J. Soc. Cosmet. Chem.*, **26**, 453 (1975).
[7] K. Nakajima, T. Yasuda, H. Nakazawa. *J. Chromatogr.*, **502**, 379 (1990).
[8] K.V. Thomas. *J. Chromatogr.*, **A833**, 105 (1999).
[9] A.F. Krivis, E.S. Gazda, T.R. Supp, M.A. Robinson. *Anal. Chem.*, **35**, 966 (1963).
[10] M.D. Seymour, D.L. Bailey. *J. Chromatogr.*, **206**, 301 (1981).
[11] H. Cheng, R.R. Gadde. *J. Chromatogr.*, **291**, 434 (1984).
[12] Y. Kondoh, S. Takano. *J. Chromatogr.*, **408**, 255 (1987).
[13] Y. Koga, M. Yoshimaru, K. Iwata. *Abstract of 50th National Meeting of The Japan Society for Analytical Chemistry,* p. 269 (2001).
[14] M. Kiyota. *Toryo no kenkyu*, **131**, 2 (1998).