Waters Alliance® LC/MS System

Analysis of Toxic Organometallic Compounds: Zn / Cu Pyrithione

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Key Words
Algaecide
Biocide
Copper Pyrithione
Zinc Pyrithione
Electrospray ionization, ESI
Toxic Compounds

Background

Zinc and copper pyrithione (ZnPT and CuPT, respectively) are widely-used biocides used in a variety of applications, such as marine paint for boats. Because the Japanese Environmental Agency (JEA) will add ZnPT to its list of toxic environmental compounds, a suitable analytical method by LC/MS was investigated and developed.

Analytical Conditions

Mass spectrometry employed the Waters ZMD, using positive electrospray ionization (ESI^+). Data was acquired in both full-scan and Selected Ion Recording (SIR) mode. HPLC utilized a Waters Alliance® HT Separations Module and a Waters Symmetry® C_{18} column (2.1x30 mm, 3.5 µm) at a flow rate of 0.3 mL/min. The following solvent program was used for separation:

Solvent A = 2mM $AcONH_4$ Solvent B= (MeOH)

Waters Alliance®HT 2790 HPLC Gradient Timetable

Time	A%	B%	Flow (mL/min)	Curve
0.00	80.0	20.0	0.30	1
10.00	0.0	100.0	0.30	6

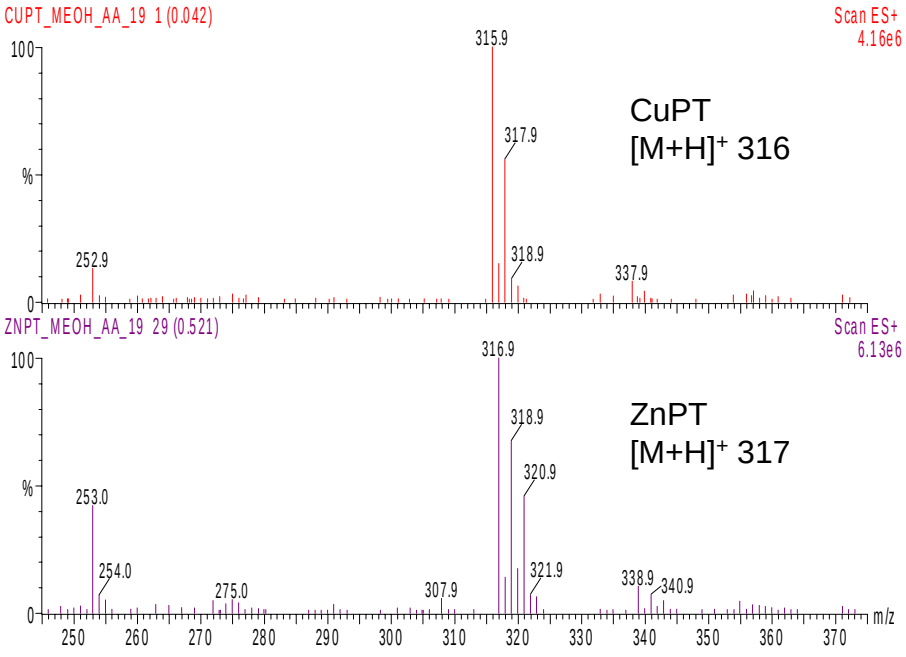


Figure 1: Mass Spectra of CuPT and ZnPT

Mass spectra of CuPT (top) and ZnPT (bottom) are shown. Both compounds give strong $[M+H]^+$ ions which differ by one mass unit. Also, note that the isotope pattern for each compound depends upon which metal is chelated.

Table 1: Mass Intensity vs. Concentration of CuPT

Name	Conc (ppb)	Rt (min)	Response	Cal. conc	%Dev
CuPT_Blank				-	
CuPT_5b	5.0	8.51	632	10.3	106.2
CuPT_10b	10.0	8.53	1332	12.6	26.5
CuPT_50b	50.0	8.56	10223	40.4	-19.2
CuPT_100b	100.0	8.56	23341	88.3	-11.7
CuPT_250b	250.0	8.56	68441	254.2	1.7
CuPT_500b	500.0	8.56	137106	501.5	0.2

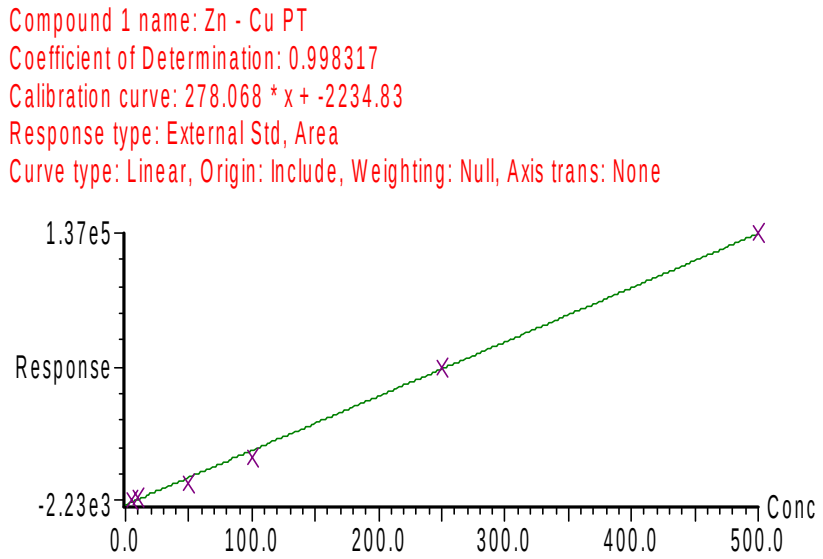
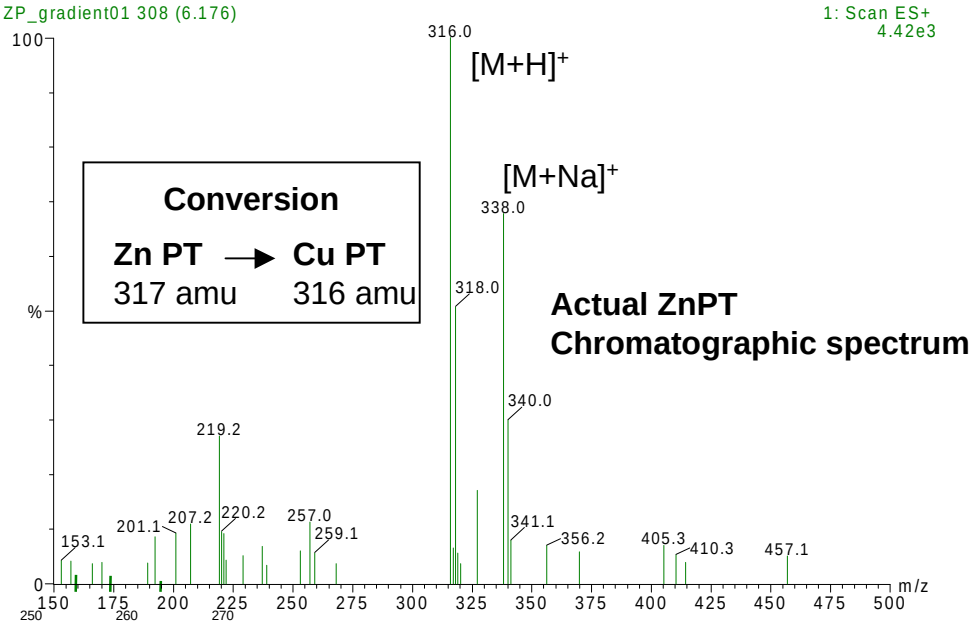


Figure 2: CuPT Calibration Curve

Analysis of a series of CuPT standards under SIR conditions (m/z 316) gave excellent linearity (left) and sensitivity over a concentration range from 5-500 ppb. The table above lists the results of this analysis.

Figure 3: Actual ZnPT Spectra
Zinc PT gave unusual results when the protonated molecular ion (m/z 317) was monitored. Additional experiments showed that ZnPT was being converted to the copper chelate when injected onto the HPLC column. This conversion was not observed when the zinc compound was flow-injected directly into the mass spectrometer.



Quantify ZnPT (as CuPT) Summary Report (5.0 - 100 ppb)

Name	Type	Std.Conc (ppb)	Rt (min)	Response	Cal. conc	%Dev
Blank_AcN_0	Blank			-		
ZnPT_5b_1	Standard	5.0	8.48	832	7.4	47
ZnPT_10b_1	Standard	10.0	8.61	1013	9.1	-9
ZnPT_25b_1	Standard	25.0	8.61	2415	22.2	-11
ZnPT_50b_1	Standard	50.0	8.61	5516	51.3	3
ZnPT_100b_1	Standard	100.0	8.61	10704	100.0	0

Compound 1 name: Zn - Cu PT
Correlation coefficient: r = 0.998681, r^2 = 0.997364
Calibration curve: 106.573 * x + 46.0665
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: Null, Axis trans: None

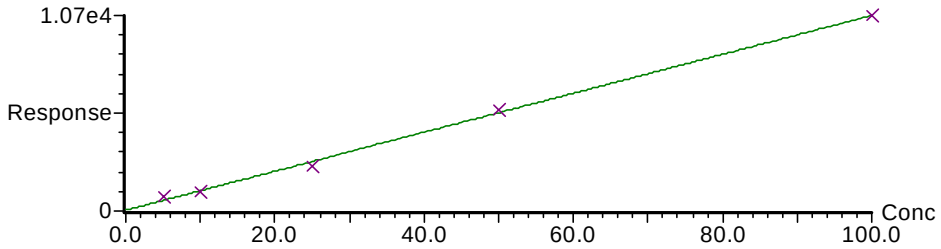


Figure 4: ZnPT Calibration Curve
When ZnPT was analyzed as the copper analogue and monitored at m/z 316, excellent linearity and sensitivity were obtained over the concentration range from 2-100 ppb. It is felt that this lower dynamic range is related to the conversion from the zinc to copper form.

25 ppb ZnPT x 7 masschromatograms (316 amu)

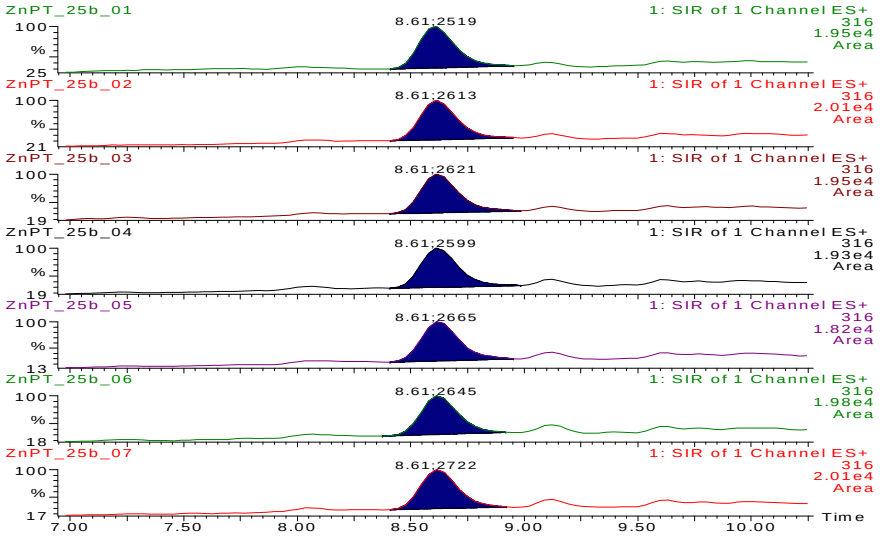


Figure 5: Replicate ZnPT Injections
Replicate injections of 25 ppb ZnPT Standard. Peak area reproducibility = 2.4% RSD.

1 ppb ZnPT Standard

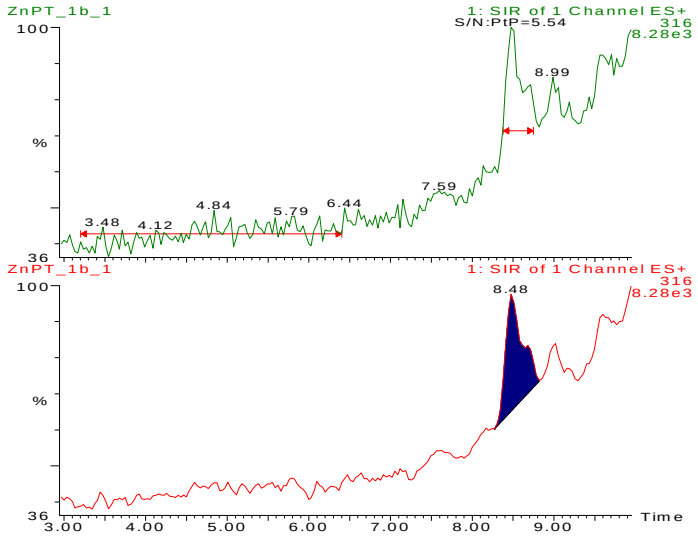


Figure 6: Signal to Noise
The signal to noise ratio at 1 ppb ZnPT standard is 5.5:1. Similar data were obtained for CuPT.

Conclusions

LC/MS offers sufficient sensitivity and linearity to detect and quantitate low ppb levels of both zinc and copper pyrithione. In addition to the quantitative power, LC/MS data clearly demonstrated the conversion of zinc pyrithione to its copper form. It is doubtful if this transformation would have been detected and elucidated with any other type of detector.

