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ISOTHIAZOLONE VOLATILITY STUDY OF A WATER BOTTOM FROM FUEL TREATED WITH KATHON® FP1.5 BIOCIDE

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Defence Research Establishment Atlantic

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ABSTRACT

An analytical method based on the gas chromatographic/mass spectrometry separation and detection of the two isothiazolones (5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one), the active ingredients in one commercially available biocide used to treat fuel systems contaminated with microbiological growth, is described. A modification of this method, to allow static headspace detection of these isothiazolones, is also described.

Results of experiments using the modified technique demonstrated that these two compounds do not volatilize from a sea water solution at temperatures up to 70°C. This suggests that undepleted isothiazolone in the water bottom of fuel tanks treated with Kathon®FP1.5 biocide would not volatilize into the habitable air space above the bilge to generate toxic components that could then be inhaled by the personnel working in the immediate vicinity.

RÉSUMÉ

On a mis au point une méthode d'analyse par chromatographie en phase gazeuse/spectrométrie de masse permettant de séparer et de détecter deux isothiazolones (5-chloro-2-méthyl-4-isothiazolin-3-one et 2-méthyl-4-isothiazolin-3-one) qui constituent les ingrédients actifs d'un biocide vendu dans le commerce et utilisé pour traiter les combustibles contaminés par des micro-organismes. Afin de mesurer la volatilité de ces substances, on a modifié la méthode pour qu'elle permette de déterminer la présence de ces isothiazolones par analyse de "l'espace de tête" en conditions statiques.

Les résultats d'expériences effectuées à l'aide de la technique modifiée ont montré que ces deux composés ne se volatilisent pas jusqu'à une température de 70°C. Ces résultats laissent supposer que l'isothiazolone qui reste dans l'eau au fond des réservoirs, dont le combustible a été traité avec le biocide Kathon® FP1.5, et qui peut entrer en contact avec des tuyaux chauds, ne se volatiliserait pas dans l'espace habitable au-dessus du fond de cale, pour donner des constituants toxiques qui pourraient alors être inhalés par les personnes travaillant immédiatement à proximité.

EXECUTIVE SUMMARY

Over the last decade some Canadian Forces (CF) ships have had significant, albeit infrequent, problems with microbiological contamination (MBC) of their shipboard fuel systems. Although eliminating fuel tank water bottoms and practicing proper fuel husbandry are the prefered and recommended means to prevent and control MBC of shipboard fuel, treatment of the affected fuel systems with a biocidal agent may be the only successful course of action in cases of severe contamination.

In an effort to identify a biocidal agent effective towards a broad range of organisms, yet safe enough for routine use, Defence Research Establishment Atlantic initiated a research program to conduct efficacy studies on commercial biocides and biostates. Pure and mixed cultures from contaminated fuel tanks were treated with the manufacturer's recommended concentrations of the biocides in fuel/water mixtures. These studies indicated that the most effective biocides were those containing chlorinated and/or unchlorinated isothiazolone compounds as the active ingredient.

One of the major concerns involved with the use of a biocide to sterilize a fuel system is the disposal of biocided water bottoms. There was concern expressed that undepleted isothiazolone biocide in the water bottom could be volatilized when it came into contact with hot piping and could then be inhaled by the personnel working in the immediate vicinity.

An analytical method based on the gas chromatographic/mass spectrometry separation and detection of the two isothiazolones in one commercially available biocide was developed, as well as a modification to this method, to allow for static headspace detection of these isothiazolones.

Results of experiments demonstrated that these two compounds do not volatilize from a sea water solution at temperatures up to 70°C. This suggests that undepleted isothiazolone in the water bottom of fuel tanks treated with Kathon®FP1.5 biocide would not volatilize into the habitable air space above the bilge to generate toxic components that could then be inhaled by the personnel working in the immediate vicinity.

TABLE OF CONTENTS

NOTATION

AMU	Atomic Mass Units
CF	Canadian Forces
°C	Degrees Celsius
GC	Gas Chromatography
ITD	Ion Trap Detector
MBC	Microbiological Contamination
mg	Milligram
mL	Milliliter
ppm	Parts Per Million
RH 651	5-Chloro-2-Methyl-4-Isothiazolin-3-One
RH 573	2-Methyl-4-Isothiazolin-3-One
µL	Microliter

1. INTRODUCTION

Over the last decade some Canadian Forces (CF) ships have had significant, albeit infrequent, problems with microbiological contamination (MBC) of their shipboard fuel systems [1,2,3]. It is well documented that MBC in a fuel system will have deleterious effects [4]. The most dramatic are filter plugging, coalescer malfunction, degradation of protective coatings and gaskets, and corrosion of exposed metal surfaces. Although eliminating fuel tank water bottoms and practicing proper fuel husbandry are the preferred and recommended means to prevent and control MBC of shipboard fuel, treatment of the affected fuel systems with a biocidal agent may be the only successful course of action in cases of severe contamination. To date biocide treatment of naval distillate fuel has been utilized only once by the CF to combat MBC in a ship's fuel system.

In an effort to identify a biocidal agent effective towards a broad range of organisms, yet safe enough for routine use, Defence Research Establishment Atlantic initiated a research program to conduct efficacy studies on commercial biocides and biostates. Several commercial products have been evaluated including compounds based on benzimidazoles, pyridinethiol-1-oxide, dioxaborinanes, morpholines and isothiazolones [5,6,7,8,9,10]. The degree of susceptibility of microorganisms, in naval distillate fuel, to the specific biocides was evaluated. Pure cultures of *Hormonoconis resinae* (previously *Cladosporium resinae*), *Yarrowia lipolytica* and *Pseudomonas aeruginosa*, and mixed cultures from contaminated fuel tanks were treated with the manufacturer's recommended concentrations of the biocides in fuel/water mixtures. Results indicated that none of the biocides tested were able to inhibit all the culture types and that biocide effectiveness was dependent upon the composition of the microbial population. However, these studies indicated that the most effective biocides were those containing isothiazolone compounds (chlorinated and/or unchlorinated) such as 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one (Figure 1) as the active ingredient. These compounds were shown to be effective at low doses against a wide variety of organisms. However, even at such low concentrations, the compounds are suspected of presenting a health hazard to humans. Unfortunately, with most commercial biocides, these two factors, efficacy and safety, rarely occur simultaneously.

One of the major concerns involved with the use of a biocide to sterilize a fuel system is the disposal of biocided water bottoms. In some cases water bottoms from fuel tanks are transferred to bilge spaces for disposal through oily water separators. Frequently, these

bilge spaces contain hot "feed water" piping which can heat the bilge water in the immediate area of the pipes. There was concern expressed that undepleted isothiazolone biocide in the water bottom could be volatilized when it came into contact with this hot piping. The volatilized biocides could then be inhaled by the personnel working in the immediate vicinity. This scenario was of prime concern during naval operations in the Persian Gulf when engine room temperatures often approached 40°C and, due to the poor quality of local petroleum distillates and the probability of embarking contaminated fuel, biocides were considered for use. Biocide use is outlined in a CF Technical Order [11] which includes very stringent controls and safeguards to reduce the health hazards to ship's personnel working in proximity to biocides, biocided fuel, fuel tank water bottoms and fuel system components containing biocided fuel or water.

This study was initiated to determine if the chlorinated and non-chlorinated isothiazolones would pose a health hazard due to volatilization at temperatures normally encountered in the bilge spaces of CF ships. This report describes the analytical procedure that was developed to enable the detection and identification of isothiazolones in air samples.

2. CONCERNS WITH BIOCIDE USE

2.1. Biocide Use on CF Ships

A number of concerns about the use and effects of biocides have been expressed by the Canadian Forces. The first is the human toxicity of the biocides. Water in the fuel tanks of gas turbine ships is stripped off by purifiers and pumped into the engine room or auxiliary machine room bilges for disposal. The water in these bilges comes in contact with warm to hot "feed-water" piping. There is concern that undepleted biocide in the water layer could enter the air space of the compartment above the bilge and be inhaled by the crew in the immediate area. There is also concern for the health of personnel who work daily with fuel system components such as filters, purifiers and coalescers that may contain biocided fuel. According to manufacturers' literature, Kathon®FP1.5 [12] may be rapidly deactivated with a solution containing 10% active sodium bisulphite, but in the undepleted state Kathon®FP1.5 is toxic to marine life and humans (Table 1). The Material Safety Data Sheet for Kathon®FP1.5 states that, as supplied, it can cause corneal damage in the eyes and produce severe skin irritation. Diluted Kathon®FP1.5 may also cause allergic skin reactions and irritation to mucus membranes in the nose and throat, and may be fatal if swallowed.

The water layer from biocide treated fuel can enter harbour waters via the discharge from fuel system purifiers and oily water separators. Due to the increasing concern over the marine environment, there is a reluctance on both coasts to use biocides, or any chemical agents that may have a detrimental effect on marine life.

The use of biocides by CF ships is approved but not recommended as the primary course of action to combat MBC in fuel systems. Eliminating fuel tank water bottoms and practicing proper fuel husbandry is the primary step toward minimizing the threat of microbiological contamination of shipboard fuel. Although these practices can control the degree of contamination present, they will not prevent MBC from occurring. Therefore, in cases of severe microbiological contamination, physical cleaning of the affected tanks and the use of a biocide may be the only recourse.

2.2. Animal Toxicity

A thirteen week subcronic inhalation study with an isothiazolone biocide produced mild mucous membrane irritation in rats exposed at a concentration of 1.15 mg/m^3 and no treatment-related effects in animals exposed at a 0.34 mg/m^3 concentration. All the effects were minor, potentially reversible, and generally reflective of minimal tissue response to a very mild low-grade respiratory irritant. Table 1 lists some of the acute toxicity data for Kathon®FP1.5 from animal toxicity testing. On the basis of these data, health and safety management personnel at one organization established an 8-hour time-weighted average workplace exposure limit of 0.1 mg/m^3 for the active isothiazolin ingredients and a 15 minute short-term exposure limit of 0.3 mg/m^3 [13].

3. DISSIPATION AND DEGRADATION OF ISOTHIAZOLONE COMPOUNDS IN THE ENVIRONMENT

Because of the significant biological activity of isothiazolone compounds against microorganisms at the ppm level, the dissipation rates of these compounds in the environment are an important concern. Studies [14,15] have been conducted to determine the rate of dissipation, the degradation pathways and degradation products of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one. These studies include the accumulation and elimination of isothiazolone compounds in rats and fish, as well as in river waters, sludge, plants and soil. Dissipation studies in Delaware River water [14] indicated that 25 percent of a 0.6 ppm concentration of the chlorinated isothiazolone remained after 25 days exposure, while the same concentration of the unchlorinated isothiazolone had totally dissipated after 14 days exposure. Further, these studies indicated

that in an aqueous environment isothiazolones are readily degraded by chemical hydrolysis, photochemical action, and biochemical mechanisms, and that the rate of degradation was pH and temperature dependent.

Studies were also conducted to isolate and identify the degradation products. The degradation pathways of chlorinated and unchlorinated isothiazolones, as derived by Krzeminski, are shown in Figure 2. Krzeminski *et al* [15] found that one of the major degradation products of chlorinated isothiazolone is N-methylmalonamic acid. N-methylmalonamic acid has a toxicity of approximately 1/50 that of the original compound.

It was concluded from the above work that "chlorinated and unchlorinated isothiazolones, used at the recommended concentrations of several parts per million, will not produce an undue ecological disturbance when discharged into the aquatic environment and that the dissipation of these compounds in the environment will occur rapidly."

4. EXPERIMENTAL

4.1. Biocides

In the most recent efficacy study [5], the two most effective biocides contained 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one as the active ingredients. Both biocides, Kathon®FP1.5 (Rohm and Haas Co.) and Isothiocide® (Specialty Chemicals Ltd.), contain 1.15 % by weight 5-chloro-2-methyl-4-isothiazolin-3-one and 0.35% by weight 2-methyl-4-isothiazolin-3-one in a dipropylene glycol carrier.

4.2. Equipment

Gas chromatography was carried out using a Varian Model 3400 capillary gas chromatograph (GC) fitted with a 30 m by 0.25 mm internal diameter DB-1 (100% methyl silicone) capillary column. The GC temperature programs used for these analyses are shown in Table 2. The detector used was a Finnigan MAT Ion Trap Detector (ITD) Model 800 using Finnigan ITDS Version 4.1 data system software containing the National Institute of Standards and Technology (formerly National Bureau of Standards) mass spectral library of 42,000 compounds. The mass detector was operated in the full scan mode over the mass range 50-650 atomic mass units (AMU) using a 1.0 second scan time (Table 2).

Samples were introduced into the GC via a heated transfer line from a Tekmar Model 7000 static headspace auto sampler fitted with a Tekmar Model 7050 fifty sample carrousel. The heated transfer line was directly coupled to the injection port of the GC using a modified septum nut and needle assembly. The sampling parameters of the headspace autosampler are shown in Table 2. The complete system set-up is shown in Figure 3.

4.3. Static Headspace Analysis

The principle of static headspace analysis is that a specific weight or volume of sample is placed in a sealed vial and heated for a fixed period of time. The volatile components of the sample diffuse into the vial's atmosphere and this atmosphere, known as the headspace, is then sampled. The components are subsequently separated, detected and identified by the GC/ITD.

4.4. Standards

Samples of pure 5-chloro-2-methyl-4-isothiazolin-3-one (RH 651) and 2-methyl-4-isothiazolin-3-one (RH 573) were obtained from Rohm and Haas Co. These pure compounds were used to make up 1.0 mg/mL standards in both hexane and filtered seawater. The hexane standards were injected directly into the GC/ITD to determine the mass spectra of each compound. The seawater standards were used to determine the retention times of each of the components using static headspace analysis.

5. RESULTS AND DISCUSSION

5.1. Analysis of Isothiazolones by Direct Injection and Static Headspace

The GC parameters (Table 2) used to determine the two isothiazolone compounds were optimized using 1.0 mg/mL standards of the pure isothiazolones in hexane. 1µL of each stock solution was injected directly into the GC and produced the reconstructed ion chromatograms shown in Figure 4. A response at scan number 682 was observed for the non-chlorinated isothiazolone and at scan number 821 for the chlorinated isothiazolone. The mass spectra for the peaks were evaluated and confirmed the chemical formulation for the isothiazolones [RH 573 (C_4H_5ONS), M+ = 115; RH 651 (C_4H_4ONSCl), M+ = 149]. Analysis of different concentrations of the two isothiazolones in hexane demonstrated that a linear relationship existed between concentration and instrument response.

The static headspace auto sampler/GC operating parameters were optimized in a similar manner.

A stock solution (1.0 mg/mL) of each of the isothiazolone in hexane was prepared. Samples of the stock solutions were placed in vials and the vials placed on the static headspace platen. The platen was heated to 100°C to volatilize the isothiazolones. The instrument (SHA/GC/MS) parameters are listed in Table 2.

The reconstructed ion chromatograms of the static headspace analysis of the standard solutions of the isothiazolones in hexane are shown in Figure 5. The retention times of the two isothiazolones are longer, when compared to the retention times for the same compounds by direct injection. Modifications to the initial GC column temperatures, hold times and column heating rates were required to ensure that the isothiazolones present in the headspace would be detected.

5.2. Analysis of Isothiazolones in Aqueous Solution

With the knowledge that both isothiazolones were separable in time under the conditions of the static headspace analysis, a stock solution of the commercially available biocide, Kathon®FP1.5, in filtered sea water was prepared. A 10 mL aliquot of a 500 ppm solution (0.5 mL Kathon®FP1.5 in 1 L filtered sea water) was placed in a 20 mL vial mounted on the static headspace auto sampler's platen. As this study was initiated to evaluate the possibility that these isothiazolones could volatilize into habitable air spaces on board ship, the initial platen temperature selected was 40°C.

No detectable response was measured for the isothiazolones at a platen temperature of 40°C. To promote volatilization of the isothiazolones from the aqueous solution the platen temperature was raised in increments of 10°C to a maximum temperature of 70°C. No response was measured. In fact, a response for the isothiazolones was only detected when concentrated Kathon®FP1.5 was placed in the vial, and then, only at a platen temperature of 100 °C.

6. CONCLUSIONS

An analytical method based on gas chromatographic/mass spectrometry was developed for the separation and detection of the two isothiazolones (5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one), which are the active ingredients in one commercially available biocide used to treat fuel systems contaminated with microbiological growth. This method was further modified for static headspace detection of these isothiazolones.

Results of experiments using the modified technique demonstrated that these two compounds do not volatilize from a sea water solution at temperatures up to 70°C. This suggests that undepleted isothiazolone in the water bottom that comes into contact with hot pipes would not volatilize into the habitable air space above the bilge to generate toxic components that can then be inhaled by the personnel working in the immediate vicinity.

TABLE 1

TOXICITY OF KATHON®FP1.5 (as supplied)

Acute oral (LD_{50}) - rats 457mg/kg

Acute dermal (LC_{50}) - rabbits 660 mg/L

Acute vapour inhalation (LC_{50}) - rats >4.62 mg/L air (nominal concentration)

Eye irritation - rabbits corrosive

Skin irritation - rabbits corrosive

Skin sensitization - guinea pigs sensitizer

EC_{50} (induction) 88 ppm ai

EC_{50} (elicitation) 429 ppm ai

TOXICITY TO WILDLIFE

Species	Conditions	LC_{50} (ai)
Bluegill	6-day exposure	0.54 mg/L
Channel catfish	6-day exposure	0.10 mg/L
Rainbow trout	6-day exposure	0.14 mg/L
Bay mussel	96 hours	1.9 mg/L
Pink Shrimp	96 hours	2.3 mg/L
Fiddler crab	96 hours	59 mg/L
Bobwhite quail	LC_{50}	97 mg/kg
Peking duck	8-day dietary LC_{50}	>100 mg/kg/day

ai - Active Ingredient

LD_{50} - lethal dose to 50% of a specified population.

LC_{50} - lethal concentration to 50% of a specified population.

EC_{50} - dosage necessary to produce any specified effect in 50% of the test population.

TABLE 2

HEADSPACE AUTO SAMPLER PARAMETERS

Platen	40, 50, 60 & 70°C
Platen Equilibrium	1 Min
Sample Equilibrium	10 Min
Vial Size	20 mL
Mixer	On
Mix Time	2 Min
Mix Power	2
Stabilize Time	2 Min
Vial Pressurization	7 psi
Pressure Time	1 Min
Pressure Equilibration	2 Min
Loop Fill	0.5 Min
Loop Equilibration	1 Min
Inject Time	0.5 Min
Valve Temp	150°C
Transfer Line Temp	150°C
Injections/Vial	1

GC PARAMETERS

	Direct Injection	Headspace Injection
Initial Column Temp	80°C	40°C
Initial Column Hold Time	2.0 Min	8.0 Min
Final Column Temp	280°C	250°C
Column Heating Rate	10°C/Min	5°C/Min
Final Column Hold Time	5 Min	5 Min
Injector Temp	275°C	250°C
Detector Temp (ITD 800)	240°C	240°C
Method Complete	27.5 Min	55 Min

ITD PARAMETERS

Mass Range	50-650 AMU
Seconds/Scan	1 Min
Acquire Time	55 Min
Multiplier Voltage	1800
Transfer Line Temp	240°C
Peak Threshold	1
Fil/Mult Delay	120 Sec
Mass Defect	100mmu/100AMU
Automatic Gain Control (AGC)	On
Background Mass	49

Figure 1. Typical isothiazolone compounds (chlorinated and/or unchlorinated) used as active biocidal ingredients, e.g. [A] 5-chloro-2-methyl-4-isothiazolin-3-one and [B] 2-methyl-4-isothiazolin-3-one.

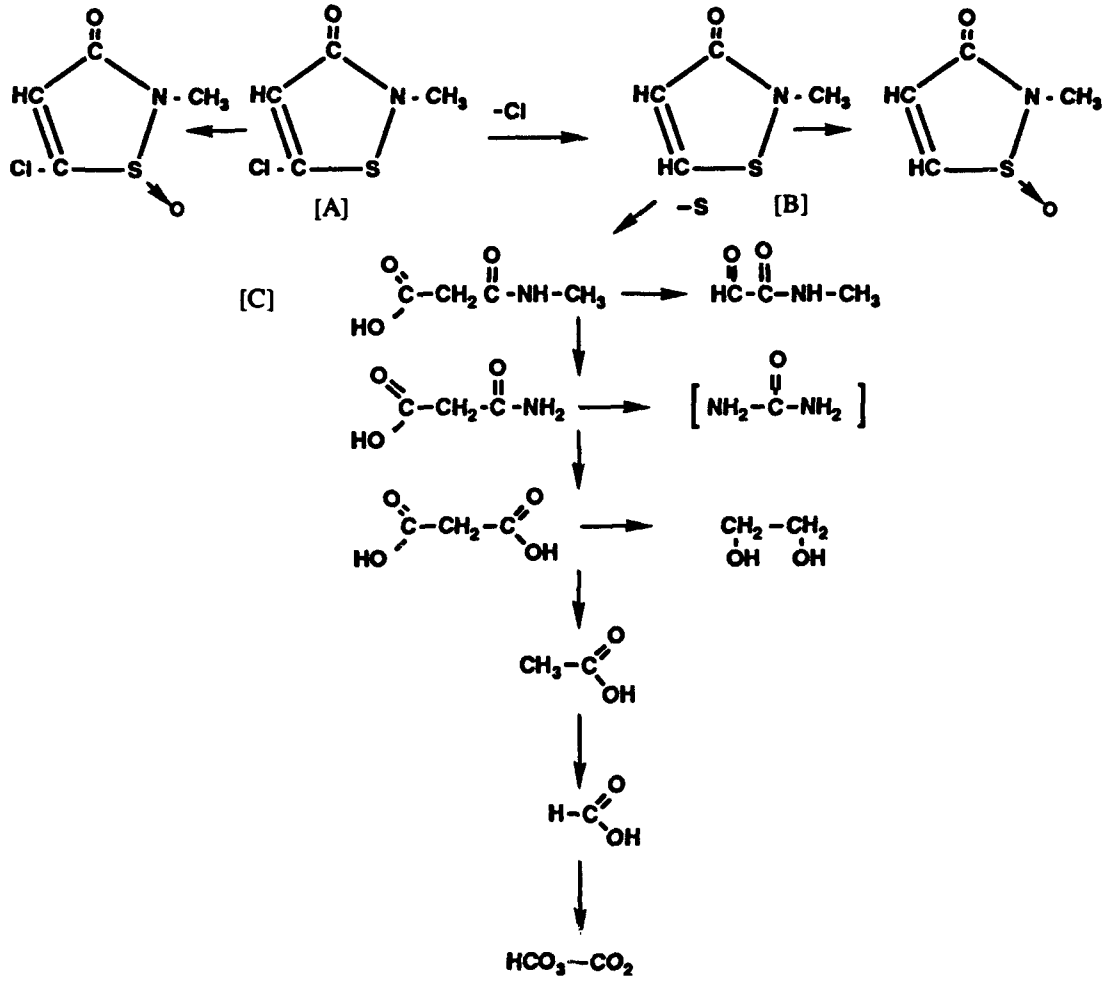

Figure 2. Degradation scheme for 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one. The major degradation pathway involves the loss of chlorine, ring opening and loss of sulfur leading to [C] N methylmalonamic acid which has a toxicity of approximately 1/50 that of the original compound.

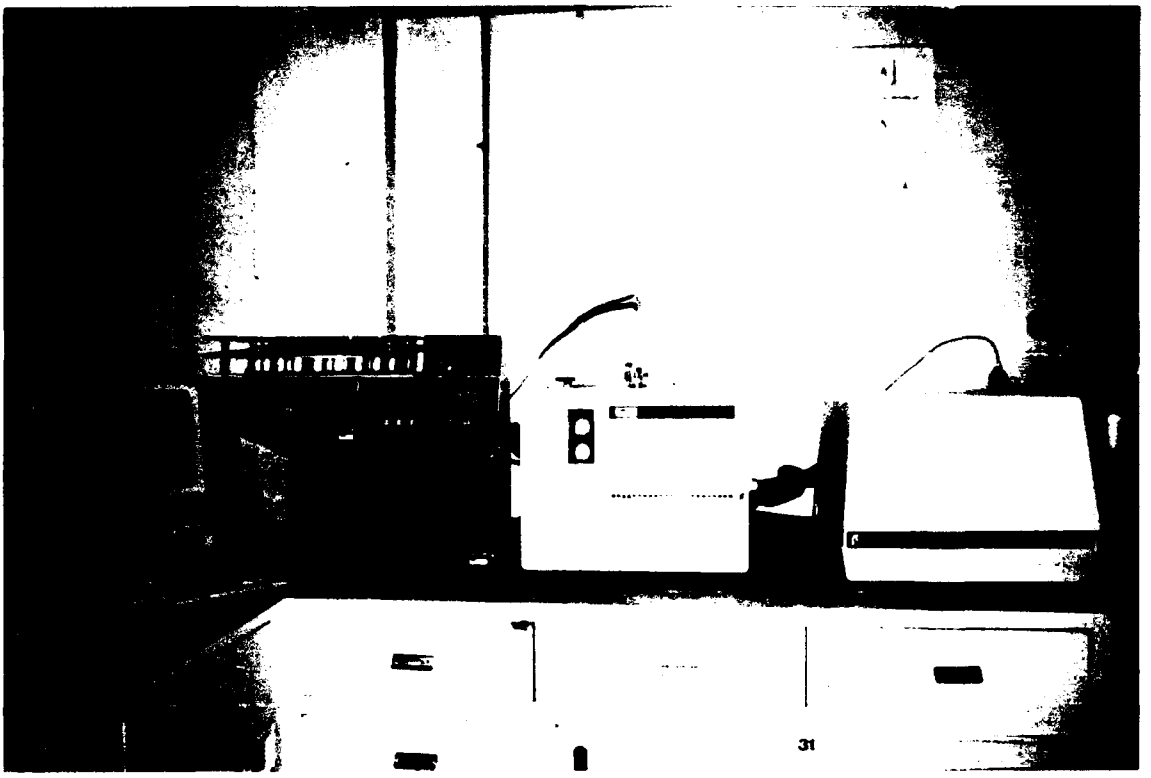

Figure 3. Complete gas chromatography/mass spectrometry system including, from left: Tekmar Model 7000 static headspace autosampler fitted with a Tekmar Model 7050 fifty sample carrousel, Varian Model 3400 capillary gas chromatograph fitted with a 30 m by 0.25 mm ID DB-1 (100% methyl silicone) capillary column and Finnigan MAT Model 800 Ion Trap Detector.

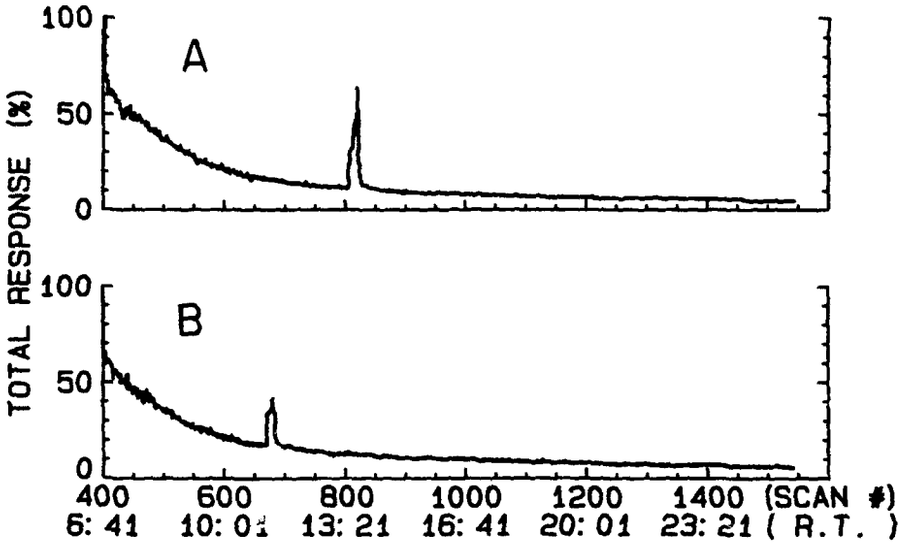

Figure 4. Reconstructed ion chromatograph of [A] pure 5-chioro-2-methyl-4-isothiazolin-3-one (RH651) and [B] 2-methyl-4-isothiazolin-3-one (RH 573) in hexane (Direct Injection).

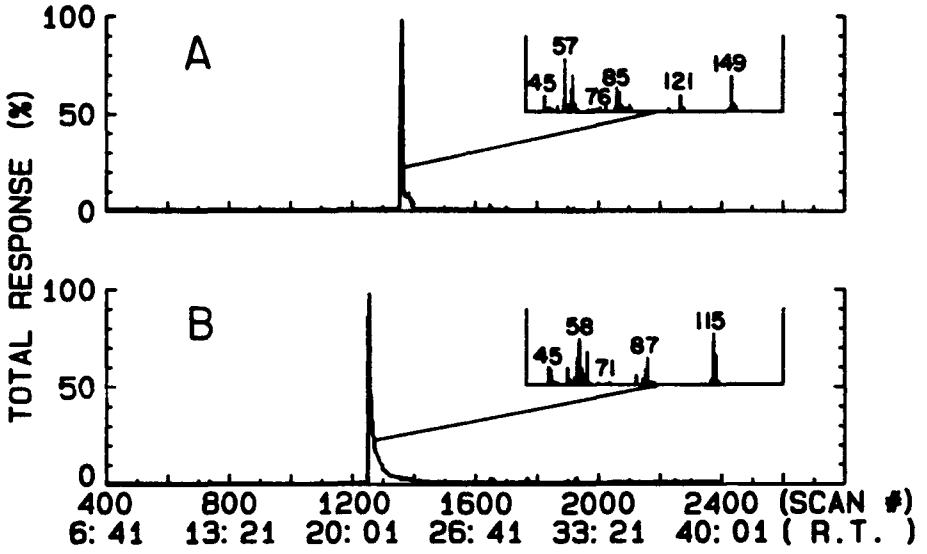

Figure 5. Reconstructed ion chromatogram of pure [A] 5-chloro-2-methyl-4-isothiazolin-3-one (RH 651) and [B] 2-methyl-4-isothiazolin-3-one (RH 573) (Headspace Injection). Included as inserts are the mass spectra for each isothiazolone.

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An analytical method based on the gas chromatographic/mass spectrometry separation and detection of the two isothiazolones (5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one), the active ingredients in one commercially available biocide used to treat fuel systems contaminated with microbiological growth, is described. A modification of this method, to allow static headspace detection of these isothiazolones, is also described.

Results of experiments using the modified technique demonstrated that these two compounds do not volatilize from a sea water solution at temperatures up to 70°C. This suggests that un-depleted isothiazolone in the water bottom, of fuel tanks treated with Kathon®FP1.5 biocide, would not volatilize into the habitable air space above the bilge to generate toxic components that could then be inhaled by the personnel working in the immediate vicinity.

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Microbiological Contamination
Isothiazolone
Kathon® FP1.5
Headspace Analysis