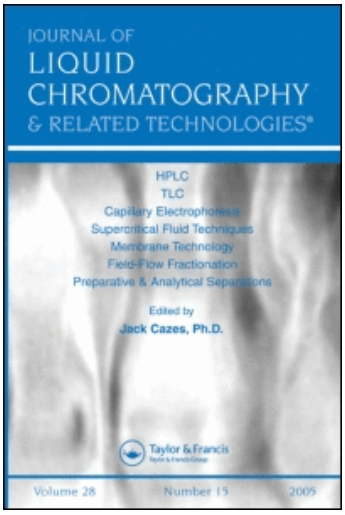

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W. Miszkiewicz[a]; P. Woszczynski[a]; J. Poskrobko[a]
[a] Synthesis Analytical Chemistry Department ul, Insitute of Heavy Organic, Kedzierzyn-Kozle, Poland

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RPHPLC METHOD FOR THE ASSAY OF 2 METHYL-4,5-TRIMETHYLENE-4-ISOTHIAZOLIN-3-ONE IN WATER-OIL EMULSIONS

WITOLD MISZKIEWICZ, PIOTR WOSZCZYNSKI, AND JAN POSKROBKO
Insitute of Heavy Organic Synthesis
Analytical Chemistry Department
ul. Energetykow 9
47-225 Kedzierzyn-Kozle, Poland

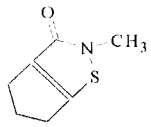
ABSTRACT

An HPLC procedure was developed for the determination of 2 Methyl 4,5-trimethylene-4-isothothiazolin-3-one in water-oil emulsions. The analytical procedure consists of the extraction in the presence of orthophosphoric acid and elution of MTI from Hypersil ODS column with acetonitrile solution of H_3PO_4 - water solution of H_3PO_4 as a mobile phase.

INTRODUCTION

Promexal W50 is a brand new preservative, from "Proxel" biocides family, for use in aqueous systems such as paints, water-oil emulsions, synthetic polymer emulsions. The main component of Promexal W50 is 2 Methyl 4,5-trimethylene-4-isothothiazolin-

3-one (MTI) patented by ICI. It prevents growth of deteriogenic species of microorganisms.



The quantity of MTI required to provide protection depends on a number of factors: susceptibility of the substrate to attack, the exposure conditions, and the product composition. The antimicrobial activity of MTI may be affected in the presence of some oxidizing and reducing agents, for example, persalts, sulphites. MTI is active only when it is present in sufficient concentrations, hence the need for an accurate and precise technique for routine analyses. The minimum inhibitory concentrations of Promexal W50 for bacteria, fungi and yeasts are between 1-40, 40-80 and 40-80 respectively [1].

An HPLC method for the assay of MTI in Promexal W50 was developed [2]. However this method can not be used directly in determination of MTI in water-oil emulsions because of the presence of interferent compounds found in the sample matrix. This creates the need of extraction.

EXPERIMENTAL

Reagents

Acetonitrile of analytical grade was obtained from Reachim (Russia) and orthophosphoric acid (85%

w/w H_3PO_4) was supplied by POCh (Poland). High purity water was obtained through HP 661A Water Purifier and MTI (purity 94.2% w/w) was purchased from ICI (UK). Samples of four emulsions with unknown MTI concentrations based on anionic-nonionic emulsifier with corrosion inhibitor (derivatives of diethanoloamine and boric acid) were from the Surfactants Department of our Institute.

Apparatus

The HPLC system consisted of a Hewlett-Packard HP 1050 liquid chromatograph equipped with an automatic solvent degasser, a Rheodyne 7125 injection valve with a 25 µl loop, and a Knauer Variable Wavelength Monitor. A personal computer and Grams/386 for Chromatography software (Galactic, Salem, NH, U.S.A.) were used for data collection and quantification of peak areas. Chromatography was carried out at a temperature of 40°C on a 200x2.1 mm steel column packed with Hypersil ODS (d_p=5µm) (Hewlett Packard) with a guard column 20x2.1 mm filled with the same material. A reciprocating shaker, type 327 (Premed, Poland) and a micro-centrifuge, type 320 (14000 rpm) (Mechanika Precyzyjna, Poland) were applied. In the preliminary studies a Hewlett-Packard HP 1090 liquid chromatograph equipped with DAD detector, and the same Rheodyne 7125 injection valve with a 25 µl loop and the same chromatographic column were used for

choosing the optimum of the gradient conditions and determination of the maximum absorption wavelength.

Procedure

2 g of H_3PO_4 was added to 20 g of a water-oil emulsion. The mixture was vigorously shaken for 20 min. Then, 2 mL of the mixture was centrifuged for 15 min at 14000 g.

20 μL of aqueous, bottom phase of the separated mixture was chromatographed under the following gradient conditions:

F = 0.3 mL/min

Gradient program:

t (min)	A (%)	B (%)
0	90	10
10	90	10
11	50	50

A = 45 mM of H_3PO_4 in H_2O,

B = 45 mM of H_3PO_4 in CH_3CN.

RESULTS AND DISCUSSION

Using DAD detector installed at HP 1090 model it was found that maximum absorption occurred at a wavelength of 270 nm (Fig.1). For the routine analysis a Knauer Variable Wavelength Monitor set at 270 nm was used.

A typical HPLC chromatogram for the MTI determination in water- oil emulsions is presented in Fig.2.

In the present study 4 samples of emulsions were analyzed for MTI content. The results are shown in Table 1.

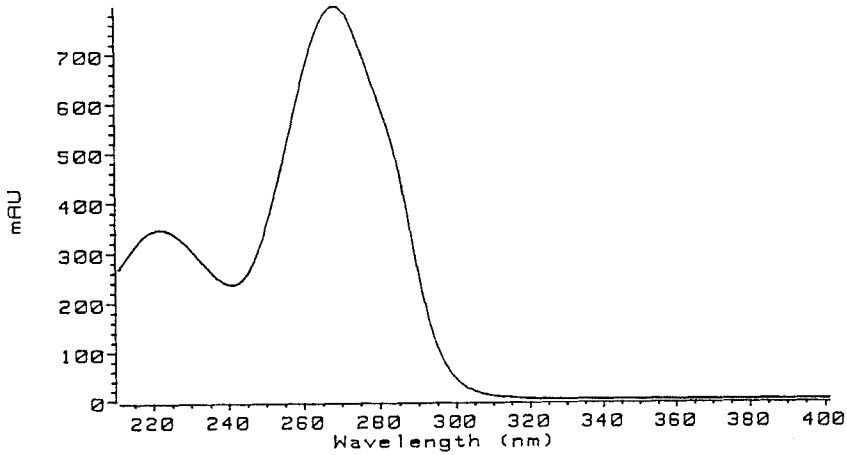


Figure 1.
UV spectra of MTI.

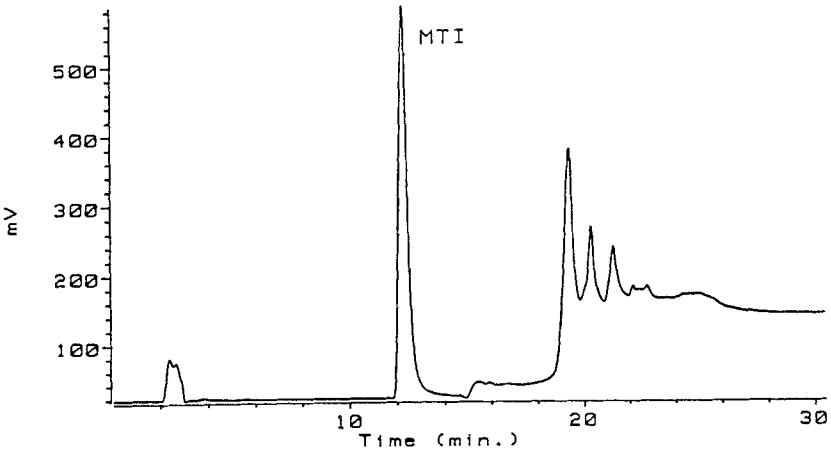


Figure 2.
RP-HPLC chromatogram of the bottom phase of a separated mixture of water-oil emulsion. Conditions of the analysis are described in the text.

Table 1. Values for the assay of MTI in water-oil emulsions.

Emulsion No	MTI, ppm (mean ± SD, n=4)
1	12.74±0.60
2	5.55±0.07
3	1.01±0.02
4	0.54±0.01

The quantitation was based on a calibration by series of dilutions from primary standard. The dependence between the peak area and the amount of MTI was determined. The regression analysis of triplicate calibration data has shown linear relationship in the 0.02 to 21.71 ppm range of MTI, with the r^2=0.9997, a=0.68 (including origin).

To estimate the efficiency of the recovery the emulsion samples were spiked with 1.5 and 14.9 µg/mL of MTI. The recovery was 96.8 and 99.2%, respectively. The yields of extraction are the mean of three replicate experiments. Reproducibility was found to be very good, and the limit of detection was estimated to be 0.01 ppm.

CONCLUSION

The method described here takes less than 50 min to perform and permits the assay of MTI at the ppm level in water-oil emulsions. No deterioration of the HPLC column was observed over several weeks of

continuous use. Because of the simple sample preparation, good accuracy and precision, the method is well suited to routine quality control analyses of commercial emulsions.

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