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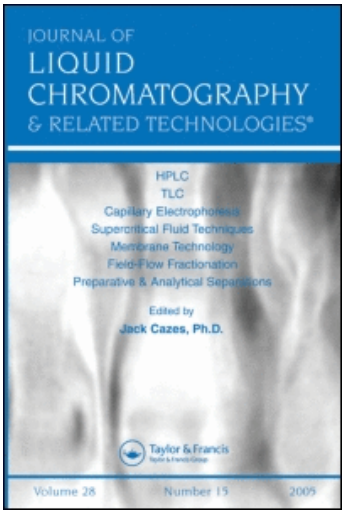

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
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The Determination of Methylene Bis-Thiocyanate by High Performance Liquid Chromatography

R. Shustina[a]; J. H. Lesser[a]
[a] Department of Analytical Research Research and Development Division, Makhteshim Chemical Works, Ltd., Beer Sheva, Israel

To cite this Article Shustina, R. and Lesser, J. H.(1984) 'The Determination of Methylene Bis-Thiocyanate by High Performance Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 7: 13, 2653 — 2658
To link to this Article: DOI: 10.1080/01483918408067032
URL: http://dx.doi.org/10.1080/01483918408067032

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JOURNAL OF LIQUID CHROMATOGRAPHY, 7(13), 2653-2658 (1984)

THE DETERMINATION OF METHYLENE BIS-THIOCYANATE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

R. Shustina and J. H. Lesser
Department of Analytical Research
Research and Development Division,
Makhteshim Chemical Works, Ltd.
Beer Sheva, 84100, Israel

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ABSTRACT

A fast, straightforward and specific method for the determination of methylene bis-thiocyanate (MBT) in technical materials and aqueous samples is described. Reversed phase high precision liquid chromatography using acetonitrile-water as eluent at a flow rate of 2 ml/min. gave a capacity factor of 2.73 for MBT. Using the method for aqueous samples allowed the determination of 2 ppm MBT by direct injection.

INTRODUCTION

Methylene bis-thiocyanate (MBT) is a fungicide and slimicide used extensively in the wood-pulp industry. It can be synthesized by mixing dibromomethane with sodium thiocyanate in an appropriate solvent (1). Methods of analysis for thiocyanates in general include those involving conversion to heavy metal derivatives (2,3), or to cyanide ion (4). Additional methods include reaction of alkyl and aryl thiocyanates with sulfide (5) and a micromethod using polysulfide (6). These methods are general, work intensive and require several hours for completion. An infrared (7,8) as well as an NMR (9) method represent instrumental analysis reported, however neither is applicable to low concentrations or to aqueous thiocyanate samples.

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A rapid and specific analytical method for the determination of MBT applicable to technical, aqueous, and low concentration samples was required. This paper presents an HPLC method for the determination of MBT which meet the above requirements.

EXPERIMENTAL

Materials and Reagents

Acetonitrile Spectroscopic grade (Aldrich Chemical Co., U.S.A.), hexane, Analytical grade (Merck, Dramstadt, FGR) and dichloromethane (Analytical grade, Frutarom, Haifa, Israel) were used. Water was distilled and passed through a Norganic cartridge (Millipore Corporation, Massachussets, U.S.A.). Technical MBT samples were supplied by Makhteshim Chemical Works, Ltd. Aqueous solutions of MBT were prepared by dissolving a quantity of technical material in water and diluting to the desired concentration. Non-aqueous technical samples were prepared by dissolving MBT in acetonitrile prior to analysis.

High Performance Liquid Chromatography

A Lichrosorb RP-18 octadecylsilane reverse phase column (Merck, Darmstadt, FGR), 12.5 cm 4.6 mm i.d. was used in a Varian model 5020 HPLC equipped with a Rheodyne model 7125 injector and UV-1 ultraviolet detector (254nm). MBT was eluted using acetonitrile: water (12:88) and a flow rate of 2 ml/min. Peak areas were integrated electronically using a Varian model CDS-111L electronic integrator and recorded using a Pantos Unicorder model U-228 (Pantos, Japan).

Linearity Study

Into a 100 ml volumetric flask was weighed 0.222 g. of MBT and acetonitrile was added to the mark. From this stock solution a series of dilutions were made ranging from 0.148 mg/ml to 2.2 mg/ml. 10 µl of these solutions were injected onto the column in duplicate. The resultant peak areas were plotted against the concentration and are represented in Figure 1.

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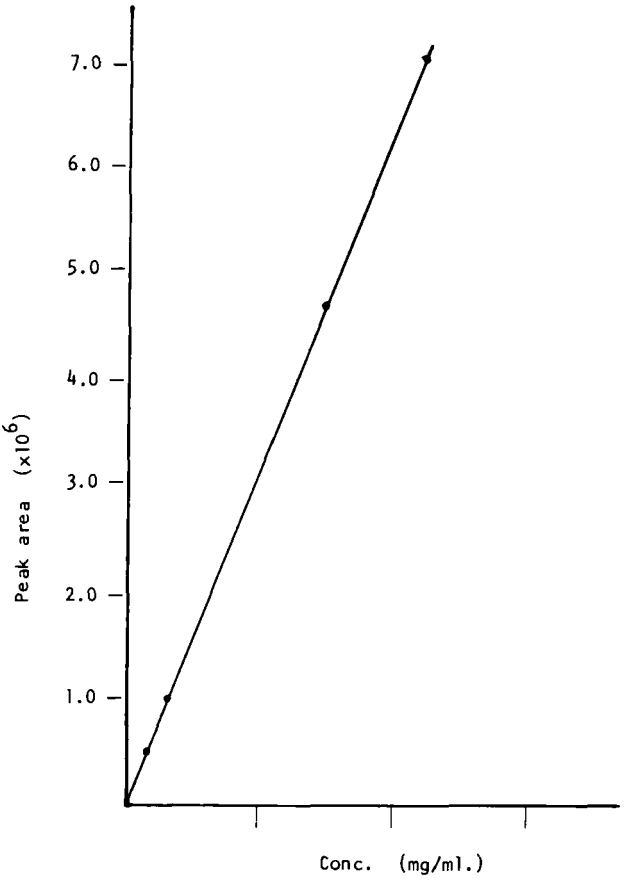

Figure 1. Curve obtained for MBT when peak area versus concentration injected was plotted.

Relative Standard Deviation

A solution of 0.139 g of MBT in 100 ml of acetonitrile was prepared and 13 successive 10 µl injections made. From the resultant peak areas the relative standard deviation was calculated.

RESULTS AND DISCUSSION

A rapid specific method for the analysis of MBT in aqueous samples and technical materials has been developed using HPLC and

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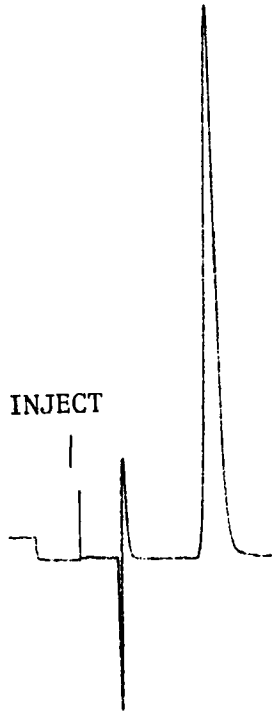

Figure 2. Typical Chromatogram of MBT

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ultraviolet detection. An octadecylsilane reversed phase column was used with an acetonitrile; water mixture as eluant. A typical chromatogram obtained using this method is shown in Figure 2. Both thiocyanate and bromide ion elute rapidly from the system and their elution time was used as the t_0 value in the capacity factor (k') calculation. The k' was calculated and found to be 2.73. Unreacted dibromomethane did not interfere with the analysis. For technical samples the total analysis time was about 10 min. When peak areas were plotted against concentration the graph shown in Figure 1 was obtained showing a linear response curve from 0.148 mg/ml to 2.2 mg/ml sample concentration. Calcul-

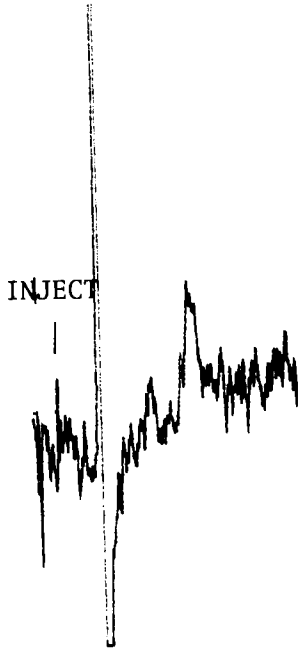

Figure 3. Chromatogram of 2 ppm MBT Aqueous Sample

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ation of the relative standard deviation yielded a value of ± 0.6% based on peak areas.

In order to confirm that the chromatographic peak represented MBT alone several samples were chromatographed on a silica column using hexane; dichloromethane (10:90) as eluent. Only a single sharp peak was observed in these instances.

Aqueous samples were filtered and injected without further workup. As little as 2 ppm (S/N>2) could be detected in this manner as shown in Figure 3. The fungicides captan, foltan and captafol did not elute under the above conditions and therefore are not potential interferents.

In conclusion a method for the analysis of MBT, applicable to aqueous and non-aqueous samples, has been presented. Method

reproducibility, linear range, and limit of detection have been established under given experimental conditions.

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