

CHROM. 14,587

## Note

---

### Determination of thiabendazole by ion-pair high-performance liquid chromatography

BARRY R. BELINKY

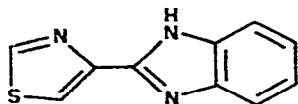
*National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226 (U.S.A.)*

(First received November 2nd, 1981; revised manuscript received November 26th, 1981)

Thiabendazole, 2-(4-thiazolyl)-1*H*-benzimidazole (TBZ), is widely used both as an anthelmintic agent for control of animal and human parasites and as a fungicide for disease control in various crops. Because of the potential for chronic exposure of workers to TBZ at the site of manufacture, it is desirable to have a sensitive and specific analytical method for low levels of this substance.

Numerous methods have been published for the determination of TBZ residues in crops using gas-liquid chromatography (GLC)<sup>1,2</sup>, thin-layer chromatography (TLC)<sup>3,4</sup>, and high-performance liquid chromatography (HPLC)<sup>5-8</sup>. However, the GLC methods require derivatization and the TLC methods are either qualitative tests or have a limited range of quantitation. The HPLC methods, as well as those using TLC or GLC, require substantial sample clean-up procedures. There have been no reports of methods for collection and analysis of airborne TBZ.

This paper presents a method for collection and analysis of particulate TBZ which requires no extensive sample clean-up when applied to industrial hygiene measurements in a manufacturing environment. At the same time the method is more sensitive and covers a wider analytical range than previously reported methods.



## EXPERIMENTAL

### Materials

HPLC-grade methanol (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) was used. Deionized water was distilled from an all-glass still. PIC reagent B-7 was purchased from Waters Associates (Milford, MA, U.S.A.). Pure thiabendazole, *N*-phenyl-4-thiazolecarboxamide hydrochloride and cyanthiazole were supplied by Merck & Company (Rahway, NJ, U.S.A.).

### Equipment

A Waters Model M6000A pump, 710B autosampler, 720 systems controller, and 440 UV detector were interfaced to a Hewlett-Packard 3354 data system. A Vydac 201 TP reversed-phase ( $C_{18}$ ) column (25 cm  $\times$  4.6 mm) was employed. The isocratic mobile phase was methanol-water (59:41) + PIC B-7 reagent prepared according to the manufacturer's directions to give a 0.005 M solution of 1-heptanesulfonic acid (pH 3.5). The flow-rate was 1.0 ml/min; the UV absorbance was measured at 313 nm.

### Sample collection and extraction

Airborne particulates were collected in the field using personal sampling pumps and 37-mm Gelman type AE glass fiber filters. Samples were collected at a flow-rate of 1.5 l/min for 2-6 h. Surface contamination was examined using Whatman No. 50 smear tabs to collect swipe samples. Both types of collection media were extracted in 20-ml scintillation vials using 5.0 ml methanol in an ultrasonic bath for 15 min and then filtered through 1.0- $\mu$ m PTFE filters.

### RESULTS AND DISCUSSION

Since common problems in the chromatographic analysis of amines are tailing on the columns and non-reproducibility of retention times, the use of an ion-pairing agent was indicated. PIC B-7 reagent (heptanesulfonic acid, pH 3.5) in methanol-water (59:41) was found to give a sharp peak for TBZ. The retention time on the  $C_{18}$  reversed-phase column was 4.60 min with a relative standard deviation (R.S.D.) of 0.5%.

A set of working standards of TBZ solutions was prepared by dissolving commercial grade TBZ in methanol, filtering, and making serial dilutions to give a concentration range of 0.2534 ng/ $\mu$ l to 253.4 ng/ $\mu$ l. Multiple aliquots of 5, 10 and 25  $\mu$ l were injected directly into the chromatograph to generate a calibration plot with a range (amount of TBZ injected) of 1.267 to 6335 ng. The calibration plot (Fig. 1) was

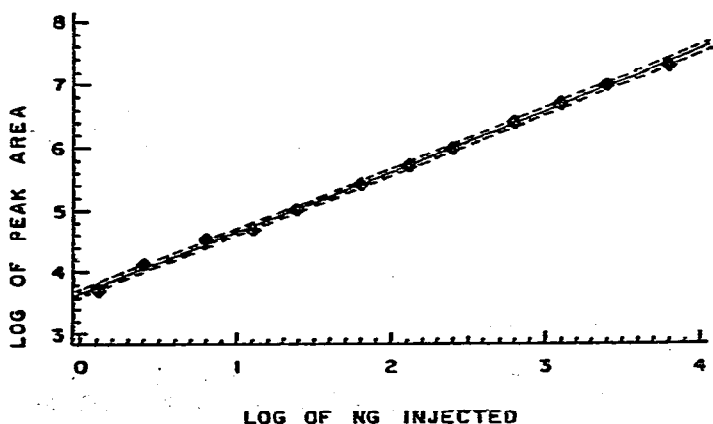


Fig. 1. Thiabendazole (TBZ) calibration curve. Range, 1.27-6335 ng. Correlation coefficient, 0.9987. Dashed lines indicate 95% confidence limits.

found to be linear over the entire range with an R.S.D. (95% confidence limit) of 4.0%. Varying the injection size from 5 to 50  $\mu\text{l}$  had no deleterious effect upon the precision.

The following chemicals, which may be used in the synthesis<sup>9</sup> of TBZ were co-chromatographed and found not to be interferences: 4-cyanothiazole, aniline and N-phenyl-4-thiazolecarboxamide hydrochloride.

Potential volatilization of TBZ from the filters during collection was checked. Two sets of filters were spiked with TBZ at four different levels each. Laboratory air was drawn through the first set of filters (using a personal sampling pump) for 5 h at a flow-rate of 1.5 l/min. Both sets of filters were then extracted and analyzed. Average recovery for both sets was 91%.

Storage stability of TBZ on glass fiber filters was examined by spiking each of eight filters with 50  $\mu\text{l}$  of a 50 ng/ $\mu\text{l}$  TBZ solution. Four were analyzed after 24 h and four after 8 days. Average recoveries were 86 and 88%, respectively.

Application of this method to field samples collected at 1.5 l/min for 6 h gives an effective range of 0.2–9000  $\mu\text{g}/\text{m}^3$ . A typical chromatogram of a sample collected in the field is shown in Fig. 2.

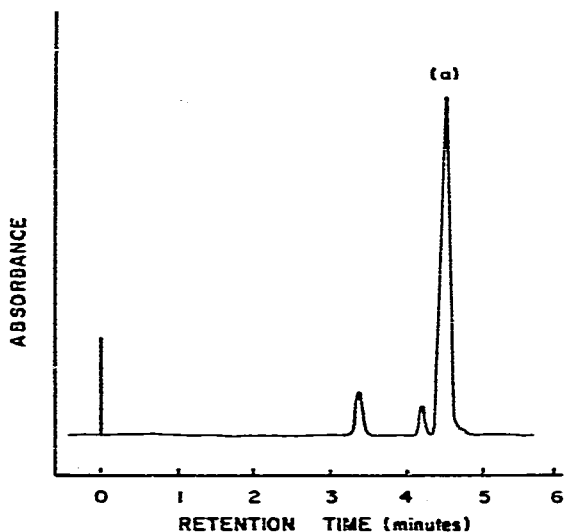


Fig. 2. Representative chromatogram of airborne thiabendazole collected on a glass fiber filter. (a) = TBZ. Solvent, methanol-water (59:41) + PIC B-7 reagent (0.005 M); flow-rate, 1.0 ml/min; detection, 313 nm, 0.05 a.u.f.s.; sample size, 50  $\mu\text{l}$ ; column, Vydac 201 TP (10  $\mu\text{m}$ ).

#### REFERENCES

- 1 A. Tanaka and Y. Fujimoto, *J. Chromatogr.*, 117 (1976) 149–160.
- 2 G. H. Tjan and J. T. A. Jansen, *Ass. Offic. Anal. Chem.*, 62 (1979) 769–773.
- 3 P. B. Baker, J. E. Farrow and R. A. Hoodless, *J. Chromatogr.*, 81 (1973) 174–177.
- 4 H. Otteneder and U. Hezel, *J. Chromatogr.*, 109 (1975) 181–187.
- 5 F. Tafuri, C. Marucchini, M. Patumi and M. Businelli, *J. Agr. Food Chem.*, 28 (1980) 1150–1153.
- 6 J. E. Farrow, R. A. Hoodless, M. Sargent and J. A. Sidwell, *Analyst (London)*, 102 (1977) 752–758.
- 7 M. Maeda and A. Tsuji, *J. Chromatogr.*, 120 (1976) 449–455.
- 8 D. J. Austin, K. A. Lord and I. H. Williams, *Pestic. Sci.*, 7 (1976) 211–212.
- 9 V. J. Grenda, R. E. Jones, G. Gal and M. Sletzing, *J. Org. Chem.*, 30 (1965) 259–261.