

CHROM. 21 033

## Note

### Determination of morpholinisulphenylbenzothiazole by high-performance liquid chromatography

M. PETRO\* and K. ĎULÁK

*Research Institute of Chemical Technology, 836 03 Bratislava (Czechoslovakia)*

(Received October 3rd, 1988)

Morpholinisulphenylbenzothiazole (BT-S-MOR) is an important industrially produced vulcanization accelerator (rubber adjuvant) available commercially under names as Vulcafor MBS, Sulfenamid M, Santocure MOR, etc.

Non-selective methods for the determination of this compound in the technical product have been reported<sup>1,2</sup>. We have found that BT-S-MOR can be determined by acidimetric titration (unpublished work). Although high-performance liquid chromatographic (HPLC) methods have been described for the determination of BT-S-MOR and its most frequently occurring impurities<sup>3,4</sup>, HPLC is not applicable to the study of the formation of this compound in aqueous medium without previous modification of the sample.

The development of reversed-phase liquid chromatographic columns for the separation of closely related compounds led us to investigate a new method for the determination of BT-S-MOR and by-products. The method can be used for checking the waste water and the composition of solid waste during the production process.

#### EXPERIMENTAL

##### *Chromatographic equipment*

All separations were carried out using a Varian Model 2210 isocratic system, which includes a Model 2010 pump, Model 2050 variable-wavelength UV detector, Model 2081 column/valve mounting module and a Rheodyne injector. Retention data and peak areas were measured and calculated by a Model SP 4200 computing integrator (Spectra-Physics).

##### *Chemicals*

The chemicals were of analytical-reagent grade. Solvents were freshly distilled before use and were purified by recommended methods<sup>5</sup>. The standards used (Table I) were prepared by the Division of Organic Chemistry in this Institute according to standard procedures. Their purities and structures were established by elemental analysis and standard physico-chemical techniques.

##### *Mobile phase*

The mobile phase was acetonitrile–ammonium acetate solution (65:35, v/v).

The solution of ammonium acetate was prepared by dissolving 6 g of anhydrous ammonium acetate in water and diluting to 1 l.

#### *Standard solutions*

Standard solutions were prepared in the range 1–10 mg per 50 ml. Stock solutions of BT-SH, BT-SO-MOR, BT-SO<sub>2</sub>-MOR, BT-MOR, BT-S-MOR and BT-S-S-MOR were first prepared by dissolving 100 mg of the appropriate compound in 50 ml of acetonitrile, then working standards were prepared by dilution of the stock solutions. The stock solutions were stable for up to 10 days when stored in a refrigerator. The refrigerated standards were brought to room temperature prior to their injection into the chromatograph.

#### *Sample solution*

For the analysis of accompanying compounds in technical BT-S-MOR, a 500-mg sample was accurately weighed into a 50-ml volumetric flask, dissolved and diluted to volume with acetonitrile. Waste water was injected directly, without dilution. All sample solutions were filtered through a 20- $\mu$ m syringe filter (Nalgene Labware) before injection on to the column.

#### *Chromatographic procedure*

The separations were performed in the isocratic mode at ambient temperature at a flow-rate of 0.8 ml/min (inlet pressure *ca.* 200 atm). Volumes of 10  $\mu$ l of the solutions were introduced on to the column with a constant-volume loop injector. The detector was operated at 280 nm (1.28 a.u.f.s.) and the chart speed was 0.25 cm/min.

#### *Calculation*

Calibration graphs were generated by plotting the peak-height ratio *versus* the concentration of standard substances in the concentration range 20–200  $\mu$ g/ml. In all instances the calibration graphs were linear with a correlation coefficient of 0.998 and passed through the origin. Values of unknown sample concentrations were determined by comparison with the calibration graph.

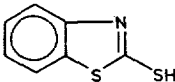
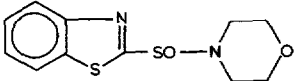
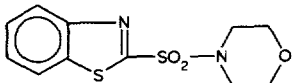
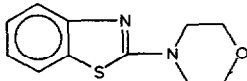
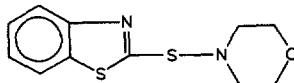
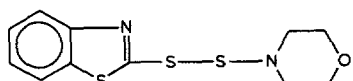
## RESULTS AND DISCUSSION

Combinations of methanol, acetonitrile and water were evaluated as mobile phases. A solvent containing acetonitrile and aqueous ammonium acetate (65:35) was found to be the most successful. This mobile phase allowed the isocratic elution of the compounds listed in Table I well within 18 min. A representative chromatogram of synthetic mixture is shown in Fig. 1.

In contrast to the most frequently occurring impurities BT-MOR and BT-SO-MOR, BT-SH<sup>6–15</sup> has its absorption maximum at 325 nm. Therefore, to achieve the maximum detectability of BT-SH it is advantageous to use dual- or variable-wavelength detection. Under the conditions used, as little as 1 mg/l of BT-S-MOR, BT-SO-MOR, BT-MOR and BT-SH can be determined in waste water without previous treatment of the sample.

In order to evaluate different analytical procedures, we compared the proposed

TABLE I  
NAMES AND STRUCTURES OF STANDARDS USED

Name	Structure	Abbreviation	Retention time (min)
2-Mercaptobenzothiazole		BT-SH	4.46
Morpholinosulphonylbenzothiazole		BT-SO-MOR	5.27
Morpholinosulphonylbenzothiazole		BT-SO <sub>2</sub> -MOR	6.06
Morpholinobenzothiazole		BT-MOR	7.01
Morpholinosulphenylbenzothiazole		BT-S-MOR	10.49
Morpholinodithiobenzothiazole		BT-S-S-MOR	16.23

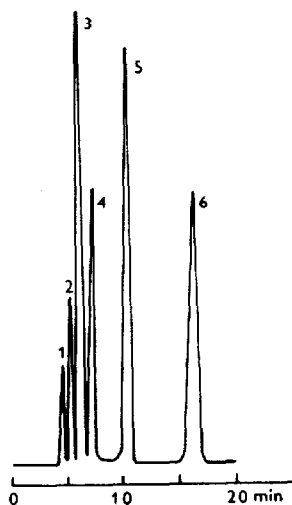


Fig. 1. High-performance liquid chromatogram of a synthetic mixture. Column, 300 × 4 mm I.D. Micro-Pak MCH-5-N-Cap; eluent, acetonitrile-ammonium acetate solution (65:35, v/v); flow-rate, 0.8 ml/min; detection, UV (280 nm). Peaks: 1 = BT-SH; 2 = BT-SO-MOR; 3 = BT-SO<sub>2</sub>-MOR; 4 = BT-MOR; 5 = BT-S-MOR; 6 = BT-S-S-MOR.

HPLC method with the titrimetric method. The latter method gave higher results.

Although the proposed method is simple, sensitive and reliable for the analysis of the technical product, of the reaction mixture in morpholine-water medium and for checking technological wastes (filtrates, distillation residues, waste water, etc.), it is not suitable for the determination of benzothiazyl disulphide (BT-S-S-BT) because of its poor solubility in polar solvents.

#### REFERENCES

- 1 N. N. Mikhailova, Z. K. Timokhina and L. A. Panova, *Zh. Anal. Khim.*, 26 (1971) 2248.
- 2 *Technical Service Report, No. LR 73/52*, Monsanto, St. Louis, MO, 1973.
- 3 S. Vertalier, M. C. Caude and J. L. Millet, *Analisis*, 7 (1979) 441.
- 4 T. F. Petrova, M. P. Ivanova and A. A. Lapschova, *Kauch. Rezina*, 12 (1983) 29.
- 5 J. A. Riddick and W. B. Bunger, *Techniques of Chemistry, Vol. II, Organic Solvents*, Wiley-Interscience, New York, 3rd ed., 1970.
- 6 W. R. Biggs and J. C. Fetzer, *J. Chromatogr.*, 260 (1983) 137.
- 7 H. Henke, *J. Chromatogr.*, 254 (1983) 296.
- 8 J. Shinohara, R. Shinohara, S. Eto and T. Hori, *Bunseki Kagaku*, 27 (1978) 716.
- 9 S. Eto, R. Shinohara, A. Kido and T. Hori, *Bunseki Kagaku*, 29 (1980) 213.
- 10 D. P. Lopes and J. A. Galoway, *J. Chromatogr. Sci.*, 20 (1982) 533.
- 11 C. B. Airando, A. Assaf, A. Gayte-Sorbier, G. Salmona and E. J. Vincent, *Anal. Chim. Acta*, 166 (1984) 221.
- 12 G. Blosczyk and H. J. Doemling, *Lebensmittelchem. Gerichtl. Chem.*, 36 (1982) 90.
- 13 J. S. Warner, T. M. Engel and P. J. Mondron, *Report, 600/4-85/026*, U.S. Environmental Protection Agency, 1985.
- 14 A. B. Sullivan, E. Morita and R. I. Leib, *Rubber World*, 195 (1986) 21.
- 15 R. N. Datta and D. K. Basu, *Rubber Chem. Technol.*, 59 (1986) 27.