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Note

Determination of 2-mercaptobenzothiazole in waste dump effluent by high-pressure liquid chromatography

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2-Mercaptobenzothiazole (MBT) has been known as a vulcanisation accelerator for rubber for many years[1]. It is also used as an intermediate for the preparation of *(inter alia)* other vulcanisation accelerators and has been demonstrated to have fungicidal properties[2].

The problem of the analysis of MBT came to our attention when samples of water which had been flowing from a refuse tip on which waste MBT was thought to have been disposed were submitted for analysis to this laboratory. A determination was required of the amount of MBT present in the samples.

The method of analysis for MBT which has been the subject of the greatest number of publications is the technique of amperometric titration, which uses metal salt solutions as titrants[3] or relies on oxidation by iodine[4] or iodine chloride[5]. Colorimetric methods have been reported in which bismuth nitrate[6] or selenious–sulphuric acid[7] are used as colour development reagents. MBT may also be determined by paper[8] and thin-layer[9,10] chromatography. Methods of analysis for the problem in hand which did not involve a separation step were deemed to be open to interference by other materials emanating from the tip, whilst thin-layer chromatographic techniques were insufficiently accurate for quantitation with the apparatus available. These problems were overcome by the development of a procedure involving the use of high-performance liquid chromatography, which resulted in a rapid and accurate method of analysis.

EXPERIMENTAL

Liquid chromatography was carried out using a chromatograph constructed in this laboratory. Mobile phase was supplied by an air-driven pressure intensification pump (Haskel, Burbank, Calif., U.S.A.) and the column was maintained at 30° by use of a water jacket and circulating thermostat (Haake, Type FE). The detector was a variable-wavelength UV monitor (Cecil Instruments, Cambridge, Great Britain) operated at a wavelength of 325 nm. Sample introduction was effected with a syringe using a stopped-flow injection system similar to that reported by Cassidy and Frei[11]. The column was constructed from stainless-steel tubing (15 cm × 4.6 mm I.D.) and was packed with Merckosorb SI 60 (5 μm) silica gel at 3,500 p.s.i. pressure from a

slurry in 2,2,4-trimethylpentane. The packing material was retained in the column by stainless-steel wire mesh of nominal pore size 8 μm (Sankey Wire Weaving, Warrington, Great Britain) inserted into a drilled-out Swagelok coupling. A similar disc of wire mesh was pressed on the top of the column packing and was retained by a plug of silanised glass wool. Ethanol–2,2,4-trimethylpentane (1:9) was used as the mobile phase with a flow-rate of 1 ml/min.

All solvents used were of spectroscopic quality (Fisons, Loughborough, Great Britain), and the MBT was reagent grade (Hopkin and Williams, Chadwell Heath, Great Britain).

The aqueous sample (2 ml) was acidified with two drops of concentrated hydrochloric acid. This mixture was shaken with chloroform (2 ml) for 1 min using a flask shaker. Aliquots (2 μl) of the chloroform layer were used for the chromatographic analysis.

RESULTS AND DISCUSSION

Several column systems were investigated for the elution of MBT. These involved adsorption chromatography using silica gel and alumina, and reversed-phase chromatography using silica gel with bonded octadecyl groups. Of these columns, silica gel gave the best results. MBT was eluted from the column in 4 min with a capacity factor (k') of 1.4 and a height equivalent to a theoretical plate (HETP) of 20 μm.

A graph plotting peak height against sample size for this system (Fig. 1) showed a rectilinear relationship between the parameters up to at least 1.5 μg MBT injected: the minimum quantity detectable (defined as a peak with height equal to three times the noise level) was 0.6 ng. This compares favourably with the limit of 0.2 μg reported for the thin-layer chromatographic procedure[10].

Two procedures were investigated for the extraction of MBT from aqueous samples. The first involved acidification of the sample followed by several extractions with chloroform: this resulted in a quantitative recovery. Similar recoveries were

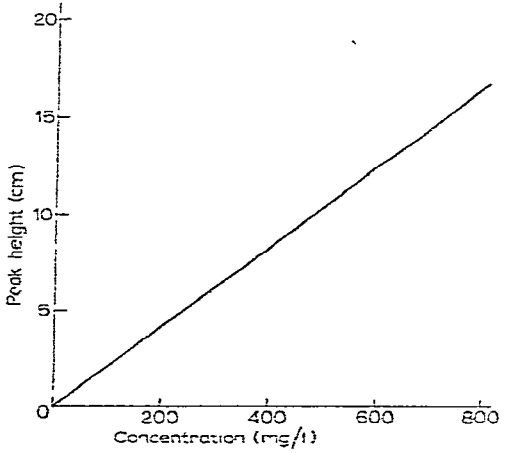

Fig. 1. Relation between peak height and concentration of MBT For conditions, see text.

also obtained by the more convenient and rapid procedure of shaking equal volumes of acidified sample and chloroform for 1 min using a flask shaker. Effluents from two sites on the waste dump were analysed for MBT using the latter extraction procedure. No peak having the retention time of MBT was observed in either sample: the concentration of MBT in the samples was hence less than 0.3 mg/l.

Fig. 2 shows chromatograms obtained for a MBT standard and those obtained for the effluent and for the effluent spiked with MBT. MBT was detected in one of the samples, however, when the sensitivity was enhanced by a factor of 10 by the extraction of 100 ml of effluent with 10 ml of chloroform. This sample gave rise to a very small peak, with a height approximately double that of the baseline noise (see Fig. 3). Whilst under these conditions an accurate determination is not possible, calculation suggests that a concentration of the order of 0.03 mg/l of MBT was present in the sample.

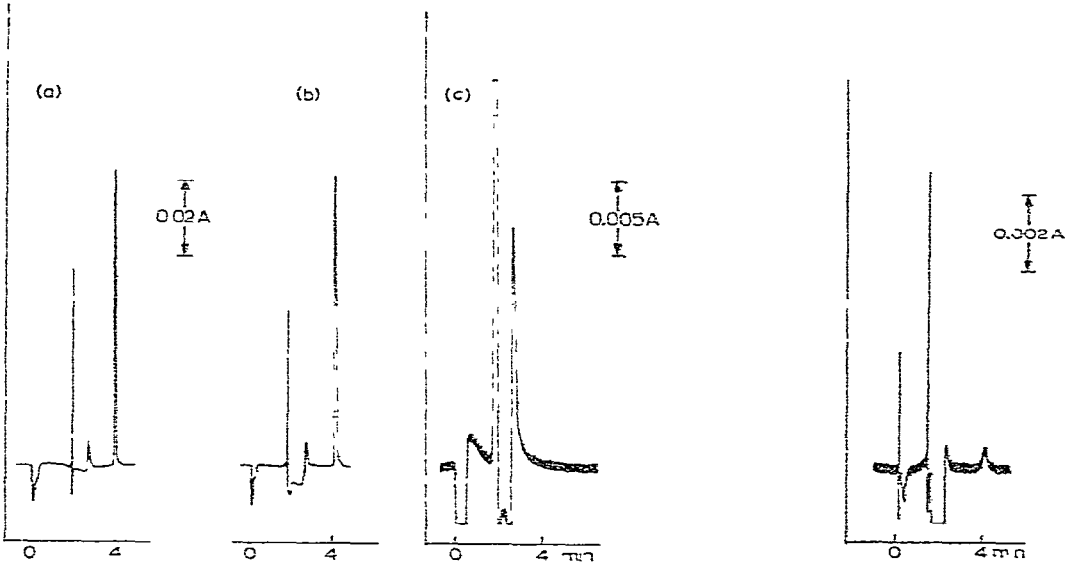

Fig. 2. Chromatography of MBT. (a) Standard, 80 mg/l. (b) Spiked effluent, 80 mg/l. (c) Unspiked effluent. For conditions, see text.

Fig. 3. Detection of MBT in effluent water. For conditions, see text.

A feature of the chromatograms is the lack of interfering peaks. Having regard to the nature of the samples, it was expected that many other components would be present in the samples. Fortunately, however, only a limited number of compounds have appreciable UV absorption at a wavelength of 325 nm, the absorption maximum of MBT: in consequence, other materials which may have been present were not detected.

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