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## RAPID CHROMATOGRAPHIC DETERMINATION OF BENZOTRIAZOLES IN AUTOMOTIVE COOLING WATERS AND COOLING WATER FORMULATIONS

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### SUMMARY

The chromatographic behaviour of benzotriazole and several of its derivatives on gas chromatographic (GC) fused-silica wall-coated open-tubular columns and reversed-phase liquid chromatographic (LC) columns is reported. Although severe tailing and irreversible retention were observed on polar GC columns, considerably improved behaviour was obtained on non-polar OV-101 and moderate polarity BP-10 columns, with detection limits (flame ionization detection) being in the nanogram range. Of the reversed-phase LC columns examined, Spherisorb 5 C<sub>8</sub> was the most suitable, producing little or no tailing. Detection limits on this column with UV detection at 254 nm were also in the nanogram range. An LC method for determining benzotriazoles in both automotive cooling waters and cooling water formulations involving only dilution of the sample prior to analysis, is described.

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### INTRODUCTION

Due to their excellent corrosion-inhibiting properties<sup>1</sup>, benzotriazole (BT) and its derivatives are widely used as additives in materials as diverse as brake fluids<sup>2</sup>, refrigerator oils<sup>3</sup>, cooling water formulations<sup>4</sup>, hydraulic fluids<sup>5</sup>, electrical insulating tapes<sup>6</sup>, anti-corrosive paper and many others<sup>7</sup>. The task of determining benzotriazoles in such materials is therefore of importance for quality control purposes. Increased emphasis will undoubtedly also be placed on the detection and quantification of these compounds in process and environmental samples in the future.

A variety of methods have been applied to the determination of benzotriazoles including potentiometry<sup>8,9</sup>, amperometry<sup>10</sup>, polarography<sup>11</sup>, non-aqueous titrimetry<sup>12</sup>, gravimetry<sup>13</sup>, indirect atomic absorption spectroscopy<sup>14</sup>, a kinetic method<sup>15</sup>,

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ultraviolet (UV) spectrophotometry<sup>16</sup>, gas chromatography (GC)<sup>8,11,17</sup>, and, more recently, liquid chromatography (LC)<sup>18-22</sup>. On specificity requirements, however, chromatographic methods offer distinct advantages for multiple determinations and the analysis of complex matrices. GC is potentially useful for determination of the benzotriazoles because of the sensitivity and selectivity of detection with the electron capture and alkali flame ionization detectors. On the other hand, BT and its derivatives display severe tailing or complete retention on packed columns<sup>17</sup>. Although this problem can be reduced by converting the benzotriazoles to their N-alkyl derivatives, fused-silica wall-coated open-tubular (WCOT) columns and reversed-phase LC appear attractive alternatives for analysis of automotive cooling waters and cooling water formulations.

On the basis of these considerations, this paper compares fused silica capillary column GC and reversed-phase LC for determining BT and its methyl, trifluoromethyl, chloro, dichloro, carboxylic acid and nitro derivatives and includes retention data and GC and LC detection limits with flame ionization detection (FID) and UV detection systems, respectively. Finally, the determination of BT and its methyl derivative by LC in a number of automotive cooling system products and cooling waters is demonstrated.

## EXPERIMENTAL

### *Reagents*

Benzotriazole (BT); 1H-6-chlorobenzotriazole (ClBT); 1H-6-nitrobenzotriazole (NO<sub>2</sub>BT); 1H-benzotriazole-6-carboxylic acid (COOHBT); 1H-6-trifluoromethylbenzotriazole (CF<sub>3</sub>BT); and 1H-5,6-dichlorobenzotriazole (Cl<sub>2</sub>BT) were prepared and purified as previously described<sup>17</sup>. Tolyltriazole (TT) was of industrial grade and contained a mixture of the isomers 1H-6-methylbenzotriazole and 1H-4-methylbenzotriazole. The compounds were prepared as 1% (w/v) in methanol and diluted as required. All solvents were supplied by Fisons Scientific Equipment and were used without further treatment other than degassing with helium.

### *Instrumentation*

UV spectra were recorded on a Pye Unicam PU8800 spectrophotometer in 1-cm quartz cells at a concentration of 16.7 mg l<sup>-1</sup> of each compound in methanol.

A Pye Unicam PU4500 capillary gas chromatograph fitted with a flame ionization detector, PU4810 computing integrator and SGE Unijector was used in the study. The WCOT columns, of fused silica (25 m × 0.22 mm I.D.) and obtained from Scientific Glass Engineering, were operated as follows: (1) OV-101 column operated at 155°C for split injection (split ratio 68:1) and, for Grob splitless injection, at 55°C for 2.5 min followed by rapid heating to 155°C. Detector and injection port temperatures were 190°C; (2) Carbowax 20M column and (3) FFAP column were both operated at 245°C (detector/injector temperature 270°C) in the split mode (split ratio 30:1); and (4) BP-10 column operated at 205°C for split injection (split ratio 68:1) and, for Grob splitless injection, at 55°C for 2.5 min followed by rapid heating to 205°C. Injection port and detector temperatures were, in both cases, 250°C. Injection volumes were 0.5 μl for split injection or 1 μl for Grob splitless injection.

LC data were collected on a Pye Unicam PU4001 gradient elution liquid chro-

matograph operated in the isocratic mode and equipped with a 20- $\mu$ l sample loop-injector and a Philips PM8252 dual-pen recorder. The commercially packed reversed-phase columns Spherisorb 5 ODS, Spherisorb 5 C<sub>8</sub> and Partisil 10 ODS2 (25 cm  $\times$  4.6 mm I.D.) were utilized in this work. All separations were carried out at 2 ml min<sup>-1</sup> flow-rate and detection was at the fixed wavelength of 254 nm. To characterize unknown chromatographic peaks in some commercial samples a PU4021 multichannel detector and PU4850 video chromatograph control centre were utilized.

#### *Analysis of commercial formulations*

Samples of automotive cooling water formulations were purchased from retail outlets in the U.K. and Australia. Cooling waters were obtained from vehicles belonging to the authors and their associates. Analysis was by LC using the Spherisorb 5 C<sub>8</sub> column with aq. methanol (50%, v/v) as mobile phase. Samples were diluted with mobile phase (typically 10%, w/w) to reduce sample viscosity prior to injection.

## RESULTS AND DISCUSSION

#### *UV spectra*

The benzotriazoles all absorbed strongly at 220 to 300 nm (Fig. 1) with molar extinction coefficients in methanol ranging from  $1.65 \times 10^4$  for NO<sub>2</sub>BT (at  $\lambda_{\max}$  235 nm) to  $5.0 \times 10^3$  for CF<sub>3</sub>BT (at  $\lambda_{\max}$  255 nm). The spectra generally consisted of two unresolved bands which, in the case of BT, have been assigned<sup>2,3</sup> to a triazole (shorter wavelength) and B<sub>2u</sub> benzenoid transition (longer wavelength).

Altering the pH of aqueous alcoholic solutions of BT produced distinct changes in the spectra. Thus, lowering the pH from 7 to 1 produced an approximately 20% decrease in absorbance without altering the position of the peak maxima. On the other hand, increasing the pH to 13 produced a single peak at 274 nm. These observations suggest the need for buffering in LC determinations with UV detection. We will comment further on this point in the analysis of the formulations.

#### *Gas chromatography*

Thermogravimetry has established<sup>17</sup> the thermal stability and volatility of the benzotriazoles at 200–300°C. Moreover, based on experience with packed columns<sup>17</sup>, the compounds were expected to elute satisfactorily from the more inert fused silica columns. Indeed, a considerable improvement in the GC of these compounds was observed on the non-polar WCOT columns. Although some tailing persisted (Fig. 2) all compounds, with the exception of the highly polar COOHBT, were readily detectable at the microgram to nanogram levels. In contrast to packed columns, however, the polar WCOT columns worsened rather than improved the benzotriazole peak shapes. Since the packed columns were silanized prior to use, an improvement in the behaviour of polar WCOT columns may be expected to accompany silanization by reduction of the number of free hydroxyl groups in the stationary phase. Moreover, the use of polar phases still seemed restricted in this application by the need to operate at temperatures above their upper limits to obtain reasonable retention times. The use of relative peak areas, rather than peak heights, in curves such as Fig. 3 enables the distinction between reversible and irreversible adsorption (and/or catalysis) to be made. Thus, on the non-polar OV-101 and BP-10 columns, irreversible

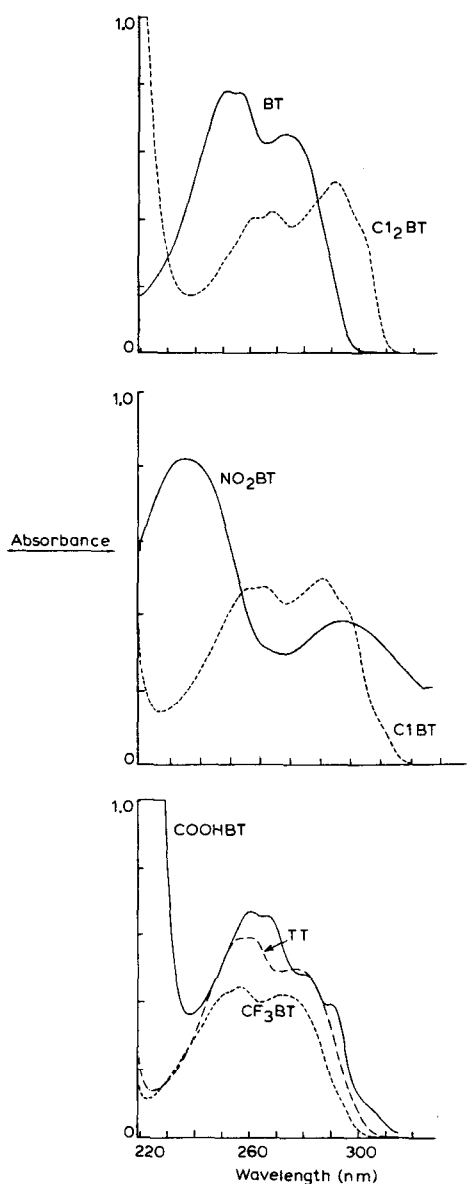


Fig. 1. UV spectra of the benzotriazoles in methanol ( $16.7 \text{ mg l}^{-1}$  except for  $\text{NO}_2\text{BT}$ ,  $8.4 \text{ mg l}^{-1}$ ).

retention was observed only at the sub-nanogram level as is evident in Fig. 3. The decrease in relative response at the higher concentrations seen in Fig. 3, especially on the OV-101 column, is attributed to inefficient sample vaporization.

Retention data and FID limits for the benzotriazoles are given in Tables I and II, respectively. Complete or near-complete separation for all compounds was achieved on all four columns, with the order of elution predictable on the basis of relative volatility<sup>17</sup>. It can be seen that the isomers of TT in the commercial product are

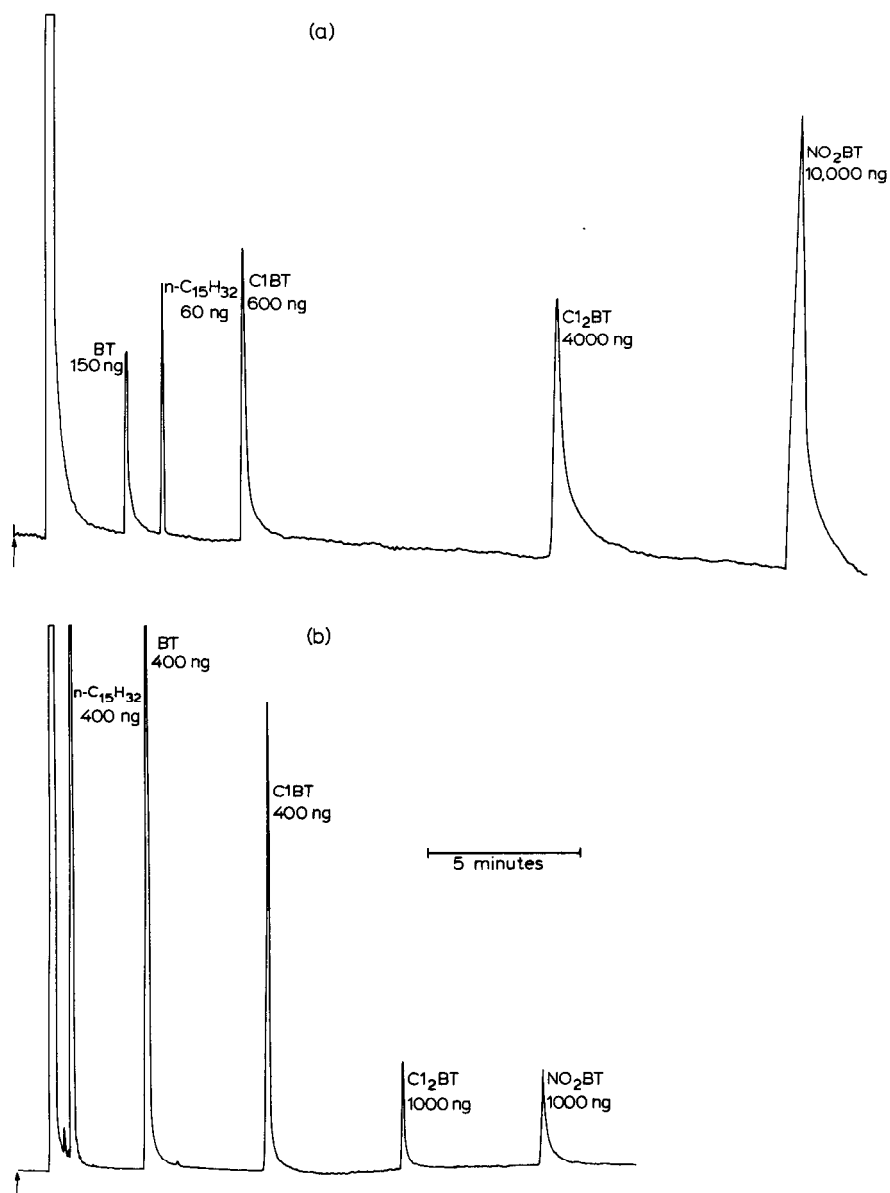


Fig. 2. Chromatograms (GC) of BT and selected derivatives with *n*-pentadecane on (a) OV-101 and (b) BP-10 using split injection. Conditions as described in Experimental except in (b) where the column was temperature programmed from 205°C, (8 min hold) at 16°C min<sup>-1</sup> to 245°C.

separated, with best resolution obtained on the polar FFAP column. The separation of these isomers may be of interest in certain situations such as characterising a particular source of TT or examining the relative fate of the isomers in a treated system. Detection limits as expected were lower with splitless injection but gave a greater precision in response compared to split mode injection ( $\pm 2.8\%$  vs.  $\pm 9\%$ ).

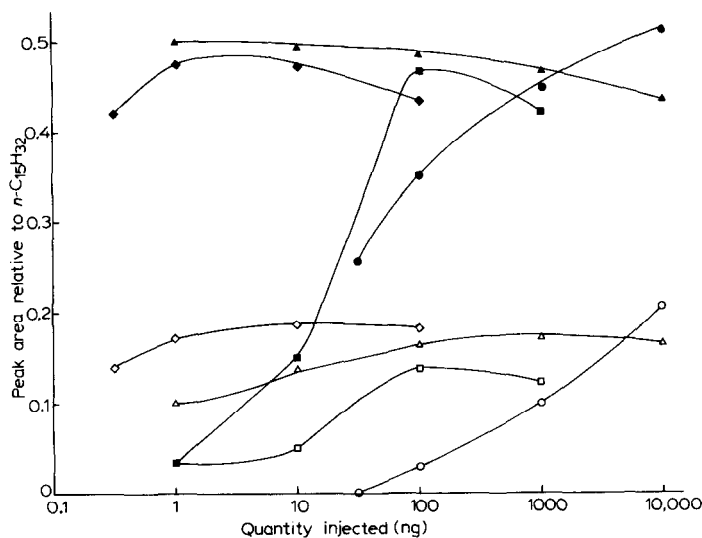


Fig. 3. Response of BT (closed symbols) and ClBT (open symbols) relative to an equal quantity of *n*-pentadecane on OV-101 (split injection, ● and ○; Grob splitless, ■ and □) and BP-10 (split injection, ▲ and △; Grob splitless, ◆ and ◇). Conditions are described in the Experimental section.

Using OV-101 and BP-10 columns together with Grob splitless injection, calibration curves of peak area vs. concentration of BT or TT were linear in the range of 0 to 25 mg l<sup>-1</sup>. However, GC analysis of the formulated products was largely unsuccessful due to overlapping peaks from the sample matrix (Fig. 4) and, more importantly, as a result of decreased column performance following repeated sample injections. Although the greater selectivity of an electron-capture detector or an alkali flame ionization detector can be expected to eliminate or reduce peak overlap, there still remains the problem of reduced column life. Suitable solvent extraction or stable stationary phases, may here, offer viable alternatives.

TABLE I

GAS CHROMATOGRAPHIC RETENTION DATA FOR BENZOTRIAZOLES

Stationary phases: OV-101, Carbowax 20M, FFAP and BP-10 with hydrogen carrier gas flow-rates of 43.5, 83.2, 42.8 and 41.7 cm sec<sup>-1</sup>, respectively and utilizing split injection. Other column conditions are described in the Experimental section.

Stationary phase	Adjusted retention time (min)					
	BT	CF <sub>3</sub> BT	TT	ClBT	Cl <sub>2</sub> BT	NO <sub>2</sub> BT
OV-101	2.5	2.8	3.4, 4.0	6.2	16.8	24.7
Carbowax 20M	3.3	4.0	3.4, 4.4	8.8	—**	—**
FFAP	10.7	10.3	10.5, 14.3	25.7	62.4	—**
BP-10	3.2	3.7	3.9, 4.6	7.2	6.0*	10.2*

\* Column temperature 240°C.

\*\* Not eluted within 60 min.

TABLE II

FID DETECTION LIMITS FOR BT AND CIBT ON OV-101, CARBOWAX 20M, FFAP AND BP-10

Conditions are as described for Table I.

Stationary phase	Detection limit (ng)	
	BT	CIBT
OV-101 — split mode	10	100
— Grob splitless	0.3	2
Carbowax 20M — split mode	20	180
FFAP — split mode	2	10
BP-10 — split mode	0.3	2
— Grob splitless	0.08	0.18

### Liquid chromatography

The highly polar nature of the benzotriazoles suggested that reversed-phase LC would be a productive approach for determining these constituents of automotive cooling water formulations. From the UV spectra of Fig. 1 it is seen that monitoring column effluent with a UV detector at 254 nm should also provide high sensitivity. Thus, UV detection limits (see Table III) were in the nanogram range and could be reduced by using variable-wavelength detection. Some preliminary work<sup>24</sup> was conducted in this direction using a diode array system (see later).

Several mobile phases comprising aqueous mixtures of acetonitrile, 2-propanol and methanol were examined to optimize the chromatographic separation. On the Spherisorb 5 C<sub>8</sub> column these solvents produced the same relative separation of benzotriazoles (Table IV). Of these, 50% aq. methanol produced the greatest selec-

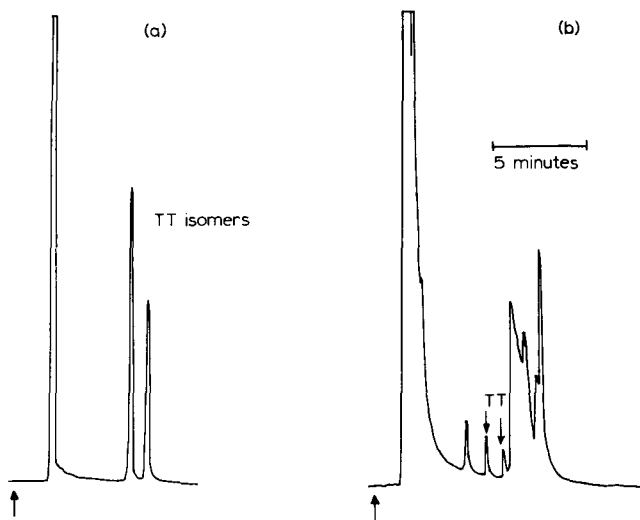


Fig. 4. Chromatograms (GC) of (a) TT (1  $\mu$ l; 0.1%, w/v) and (b) Motorcraft Antifreeze-Plus Antifreeze (1  $\mu$ l; 10%, w/v) on OV-101 column using split injection. Conditions as described in the Experimental section.

TABLE III

## LIQUID CHROMATOGRAPHIC RETENTION DATA AND DETECTION LIMITS FOR THE BENZOTRIAZOLES AT 254 nm

Mobile phases: 42% aq. methanol (for Spherisorb 5 ODS) and 50% aqueous methanol (for Partisil 10 ODS 2 and Spherisorb 5 C<sub>8</sub>).

Compound	Spherisorb 5 ODS		Spherisorb 5 C <sub>8</sub>		Partisil 10 ODS 2
	Retention time (min)	Detection limit (ng)	Retention time (min)	Detection limit (ng)	Retention time (min)
COOHBT	1.7	0.35	1.9	0.3	2.5
NO <sub>2</sub> BT	3.9	0.45	2.5	0.6	3.9
BT	4.6	0.45	2.8	0.6	2.9
TT	7.3	1.2	3.5	1.0	4.7
CIBT	8.5	2.3	4.3	1.3	6.1
CF <sub>3</sub> BT	11.6	2.3	6.1	1.3	8.4
Cl <sub>2</sub> BT	17.2	4.7	8.2	2.0	14.5

tivity (largest spread of retentions). Since this solvent also generated the best peak shapes and reproducibility it was utilized for all further work.

Although complete separation of the seven benzotriazoles was possible on the three columns examined using aq. methanol as mobile phase (Fig. 5), severe tailing was obtained on Partisil 10 ODS2 and, to a lesser extent, on Spherisorb 5 ODS. In addition, COOHBT eluted prior to the solvent peak. The addition of perchloric acid (0.5%, v/v) to the mobile phase eliminated this problem and reduced the extent of peak tailing, possibly due to suppressed ionization of the COOHBT. However, the increased acidity of the mobile phase had a detrimental effect on column life. Of the three columns studied, Spherisorb 5 C<sub>8</sub> provided the best separation of benzotriazoles

TABLE IV

RETENTION TIMES OF BENZOTRIAZOLES ON SPHERISORB 5 C<sub>8</sub> WITH VARIOUS MOBILE PHASES

Flow-rate was 2.0 ml min<sup>-1</sup> except for propanol-water, 1.7 ml min<sup>-1</sup>.

Compound	Retention time (min)		
	Acetonitrile-water (50:50)	Propan-2-ol-water (45:55)	Methanol-water (50:50)
COOHBT	1.28	1.45	1.9
NO <sub>2</sub> BT	1.63	1.70	2.5
BT	1.61	2.05	2.8
TT	1.73	2.15	3.5
CIBT	1.81	2.24	4.3
CF <sub>3</sub> BT	2.04	2.37	6.1
Cl <sub>2</sub> BT	2.15	2.44	8.2



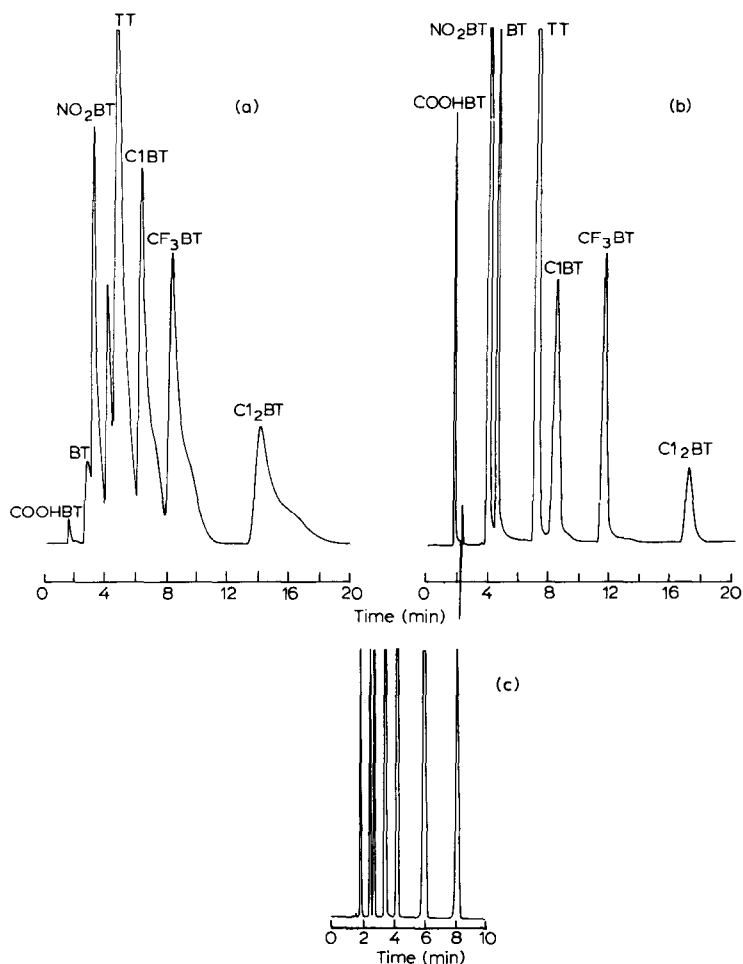


Fig. 5. Chromatograms (LC) of COOHBT ( $17 \mu\text{g ml}^{-1}$ ), NO<sub>2</sub>BT and BT ( $34 \mu\text{g ml}^{-1}$ ), and TT, C1BT, CF<sub>3</sub>BT and C1<sub>2</sub>BT ( $117 \mu\text{g ml}^{-1}$ ) on (a) Partisil 10 ODS<sub>2</sub>, (b) Spherisorb 5 ODS and (c) Spherisorb 5 C<sub>8</sub>. Conditions as for Table III.

producing little or no peak tailing (Fig. 5). Separation of the isomers of TT was also possible by careful adjustment of the composition of mobile phase.

## CONCLUSIONS

LC rather than GC was selected for analysis of automotive cooling water formulations because of minimal sample preparation, requiring only dilution, and the potential for simultaneously determining other inhibitors such as mercaptobenzothiazole (MBT) and benzoate. External calibration offered acceptable precision ( $\pm 1.9\%$ ) and was adopted for simplicity although internal standardization should provide better precision. For BT, TT and MBT, calibration curves of peak height or area vs. concentration were linear in the range of 0 to  $140 \text{ mg l}^{-1}$  (Fig. 6). Analysis

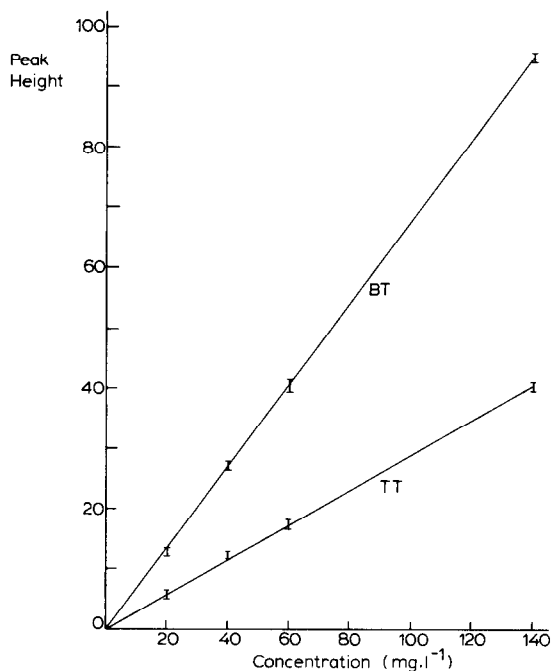


Fig. 6. Calibration curves for BT and TT using fixed-wavelength detection at 254 nm.

TABLE V

BT AND TT CONCENTRATIONS IN COMMERCIAL ANTIFREEZE FORMULATIONS AND OF SAMPLES SPIKED TO THE STATED CONCENTRATION OF EITHER BT OR TT

Results are expressed as the mean and standard deviation of 5 replicate determinations.

Sample	Concentration (% w/v)	
	BT	TT
Fiat Parafu	0.026 ± 0.002	0
Motocraft Antifreeze-Plus Antifreeze	0	0.11 ± 0.01
Motorcraft Super-Plus Antifreeze	0	0.12 ± 0.01
Toyota Forlife	0	0.018 ± 0.002
Catoleum Afluc 2001	0	0.84 ± 0.03
Repc Woodhill Radiator Rust Inhibitor*	0	0
Castrol Radiator Corrosion Inhibitor	0	1.59 ± 0.02
Wynn's X-Tend Radiator Treatment	1.64 ± 0.03	0
BP Antifrost Antiboil	0	0.15 ± 0.01
Toyota Radiator Conditioner	0.72 ± 0.02	0
Fiat Parafu + 0.005% TT	0.026 ± 0.002	0.0051
Fiat Parafu + 0.15% TT	0.026 ± 0.002	0.15 ± 0.01
Toyota Forlife + 0.005% BT	0.0052	0.018 ± 0.002
Toyota Forlife + 0.050% BT	0.048 ± 0.001	0.018 ± 0.002

\* Sample contains 2.87% (w/v) MBT (retention time: 5.1 min).

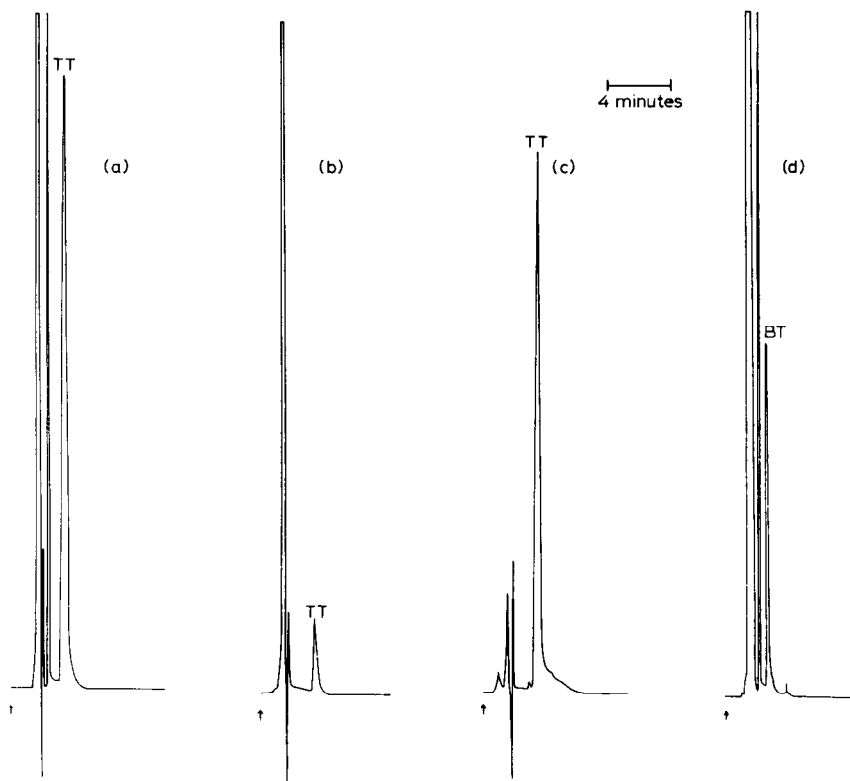


Fig. 7. Chromatograms (LC) of commercial antifreeze formulations showing the presence of TT in Motorcraft Super-Plus Antifreeze (a), Toyota Forlife (b), Motorcraft Antifreeze-Plus Antifreeze (c), and BT in Fiat Paraflu (d).

time for triplicate determinations was less than 12 min (18 min when MBT was present). Results for the analysis of several commercial samples are given in Table V with concentrations varying from 0 to 1.64% (w/v). Chromatograms (Fig. 7) demonstrate the presence of either BT or TT in the formulations with none containing both BT and TT. One sample contained MBT but no BT or TT which suggests that this formulation is unsuitable for automotive engines containing aluminium alloy components. An interesting distinction between the U.K. and Australian formulations arises in that the latter are characterized by a higher concentration of corrosion inhibitor. The identity of the two benzotriazoles was confirmed in the formulations from their UV spectra obtained with the diode array multichannel detector. Recovery experiments involved spiking two of the commercial samples with known concentrations of either BT or TT and re-analysing the samples. The results showed recoveries of between 95% and 104% (see Table V). Buffering of the mobile phase appeared unnecessary despite the pH dependence of the UV spectra. It should be pointed out that most formulations of the type examined are heavily fortified with borate or phosphate buffers. Obviously the buffering action of formulations occurs only in the sample before injection and not in the mobile phase itself. However, it is the form at the point of injection that is important as the solvent should have no effect on equilibrium except to dilute acidic or basic components.

The method was also applied to the determination of BT and TT in automotive cooling systems with suitable modification to allow for the generally lower concentration of these compounds in such systems. Although precision was marginally poorer than for the formulated products, results were in the expected range allowing for the recommended dilutions of the various formulations in use.

Finally, the LC method is also suitable for the determination of nitrite in such samples following derivatisation to a benzotriazole as previously described<sup>17</sup>. Further work is currently in progress aimed at determining benzotriazole in other products, examining temporal changes in the level of BT and TT in treated systems, and analysing process and environmental samples for BT and TT.

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