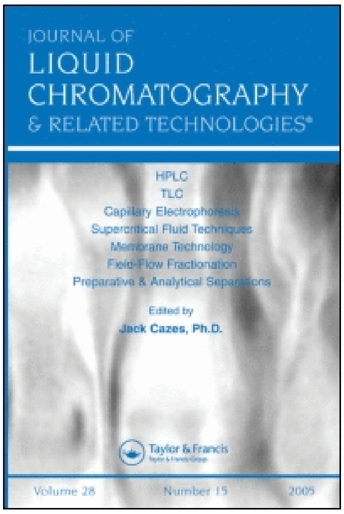

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DETERMINATION OF SODIUM TOLYLTRIAZOLE AND SODIUM MERCAPTOBENZOTHIAZOLE IN ENGINE COOLANTS

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ABSTRACT

A high performance liquid chromatography method was developed to quantitatively determine the corrosion inhibitors sodium tolyltriazole and sodium mercaptobenzothiazole in fresh and used ethylene glycol-based engine coolant formulations. Aliquots of coolant, diluted with water and methanol, are analyzed directly. Approximately one-half hour is required to determine both inhibitors with relative standard deviations of about 4 %.

INTRODUCTION

Automotive engine coolants require inhibitors to prevent corrosion of components in contact with the coolant. Two widely used inhibitors are tolyltriazole (TTA) and mercaptobenzothiazole (MBT), present as the sodium salts. These compounds may be used individually or in combination in various ethylene glycol-based engine coolant formulations.

Several gravimetric and photometric methods had previously been developed for the determination of TTA (1) and MBT (2). However, TTA and MBT interfere with one another in these methods. High performance liquid chromatography (HPLC) has been used successfully

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to determine TTA in cooling water (3) and engine coolants (1), but MBT was not determined. Hence, these methods were unsuitable for our purposes, and a new method utilizing HPLC was developed to determine both TTA and MBT. In addition the newly developed method can be extended to determine benzotriazole (BTA) and benzoate, two components which occasionally are added to engine coolants.

During the course of this work, a recent publication (4), which discussed the determination of TTA, MBT, and BTA in engine coolants, was found. The published procedure used a similar HPLC method. However, the method was shown to be applicable only to fresh formulations, whereas the method presented in this report can be applied to both fresh and used engine coolants.

EXPERIMENTAL

Apparatus All high performance liquid chromatography (HPLC) separations were performed on a Varian Model 5060 liquid chromatograph (Varian Associates, Palo Alto, CA) equipped with a Perkin-Elmer Model LC-75 ultraviolet detector (Perkin-Elmer, Norwalk, CT) set at 254 nm. Peak areas were measured with a Hewlett-Packard Model HP 3390A integrator (Hewlett-Packard, Avondale, PA). Injections into the liquid chromatograph were made with a Valco injection valve (Valco, Houston, TX) equipped with a 30-μL loop. The liquid chromatographic column was a 25 cm x 4.6 mm Zorbax ODS (duPont Instruments, Wilmington, DE). The column was protected with a Rheodyne 2-μm column inlet filter (Rainin Inst. Co., Woburn, MA). Other apparatus included standard laboratory glassware such as pipets and volumetric flasks.

Standards and Reagents Methanol used for sample preparation and HPLC separations was HPLC grade (J. T. Baker, Phillipsburg, NJ). Deionized water was also used for sample preparation and HPLC separations. Standards were prepared by dissolving 100 mg of tolyltriazole (TTA) (Sherwin Williams Chemicals, Cleveland, OH) in 100 mL of methanol, and 1.00 g of 50 % sodium mercaptobenzothiazole (NaMBT), R. T. Vanderbilt Co., Inc., Norwalk, CT) in 100 mL of methanol or 500 mg of mercaptobenzothazole (MBT) in 100 mL of methanol. Calibration solutions were prepared from the standard solutions to contain 0.06 mg/mL TTA, 0.4 mg/mL NaMBT or 0.2 mg/mL MBT; 0.04 mg/mL TTA, 0.2 mg/mL NaMBT or 0.1 mg/mL MBT; and 0.02 mg/mL TTA, 0.1 mg/mL NaMBT or 0.05 mg/mL MBT. All calibration solutions contained 40 mL of water per 100 mL final solution. Solutions were diluted to volume with methanol and mixed. Calibration solutions were stable for at least one week.

Procedure Engine coolant samples (fresh, 2 mL; used, 4 mL) were aliquoted into 50 mL volumetric flasks. Pipets were allowed to drain for at least 3 min. Alternately, samples can be weighed. Water (20 mL for fresh samples, 18 mL for used samples) was added; solutions were diluted with methanol and mixed.

Aliquots of samples or calibration solutions were injected onto the HPLC column and eluted with the following mobile phase scheme at 25°C: 55 % methanol/45 % water at 1 mL/min for 10 min; step to 100 % methanol in 1 min, hold for 3 min, then step to 2 mL/min, hold for 3 min; step to 55 % methanol in 1 min and hold for 5 min; step to 1 mL/min before next injection. Identification of TTA and MBT was based on comparisons of retention times with standards. Under these conditions TTA eluted at 7.2 min, and MBT eluted at 10.2 min. (Addition of acetic acid (0.5 %) to the methanol may be required on some Zorbax ODS columns to obtain the indicated resolution for TTA and MBT.) For used coolant samples identification of MBT was also based on retention times of spikes. Quantitation was made by comparing peak areas of the TTA or MBT ultraviolet signals to those of external calibration solutions.

RESULTS AND DISCUSSION

Sample Preparation Samples and calibration solutions were diluted with a mixture of 40 % water in methanol to approximate the HPLC mobile phase. When methanol alone was used to dilute samples, reduction in peak heights (but not areas) occurred and salts precipitated from solution. Aliquots of used engine coolants were selected to bring TTA and MBT concentrations within the range of the calibration solutions. Solid particulates in dilutions of used formulations were allowed to settle before removing samples for analyses.

High Performance Liquid Chromatography It was decided that the most straight-forward approach to analyze dilute engine coolants was reverse phase high performance liquid chromatography with ultraviolet detection. Figure 1 shows a chromatogram of a typical engine

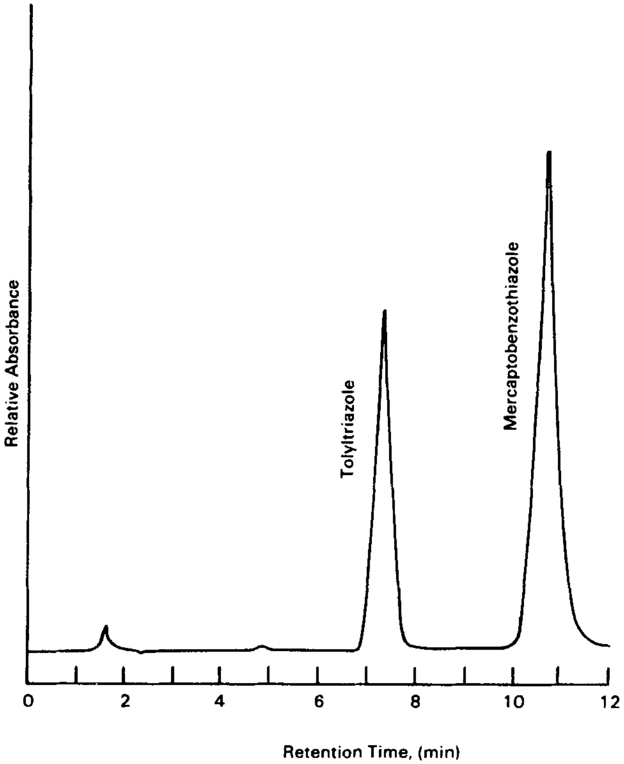

Figure 1. Chromatogram of diluted engine coolant using Zorbax ODS column, 55 % methanol/45 % water mobile phase at 1 mL/min and UV detection at 254 nm, 0.32 AUFS.

coolant formulation. Ultraviolet absorbance measurements were made at 254 nm because of the general availability of fixed wavelength detectors. Although TTA exhibited an absorbance maximum at 258 nm and MBT exhibited maxima at 232 and 324 nm, adequate sensitivity for both is obtained at 254 nm.

A mixture of methanol (55 %) and water (45 %) was found suitable to separate TTA and MBT. In addition benzotriazole (BTA) and benzoate, other additives less commonly found in engine coolants, can also be detected with this method. Figure 2 depicts a chromatogram showing separation of benzoate, BTA, TTA, and MBT. Columns were rinsed with 100 % methanol after each run to remove contaminants.

Identification of TTA and MBT was based on retention times. Retention times for TTA varied little (± 0.1 min) from sample to sample. However, retention times varied considerably (as much as ± 0.6 min) for MBT. For fresh samples this variance in retention time posed no problem. However, used samples often had to be spiked

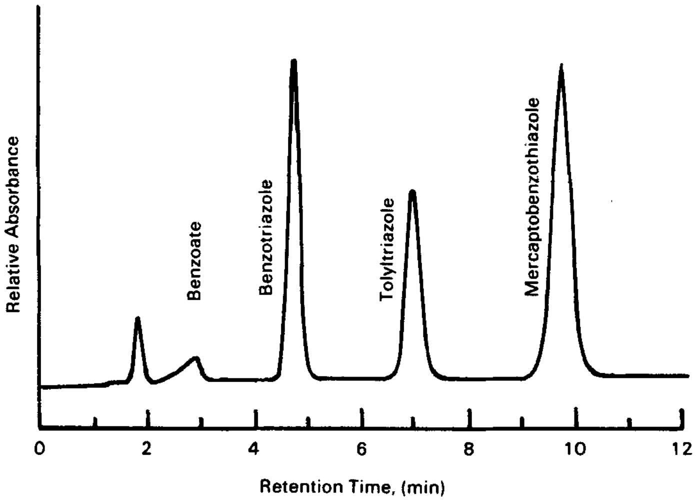

Figure 2. Chromatogram showing separation of benzoate, BTA, TTA, and MBT using Zorbax ODS column, 55 % methanol/45 % water mobile phase at 1 mL/min and UV detection at 254 nm, 0.32 AUFS.

for positive identification of MBT because other peaks, presumably from degradation products, were present in the vicinity of the MBT peak.

Peak areas were used to calculate concentrations; peak height calculations were satisfactory, although slightly poorer precision resulted. Peak areas for TTA calibration solutions were nearly constant throughout an 8-hour run, however peak areas for MBT varied by as much as 10 %. The largest deviation occurred during the first couple of runs, hence, columns were preconditioned by running one or two sample solutions prior to obtaining data. In addition, the most concentrated calibration solution was run after each 4 to 5 samples to measure any instrumental response changes for MBT. The cause for this variance is unknown.

Method Evaluation To evaluate the precision of this method, 10 aliquots of an experimental fresh engine coolant were processed using this procedure. Relative standard deviations when using peak areas to calculate concentrations were 3.6 % and 3.1 % for TTA and MBT, respectively. When using peak heights, measured from a strip chart recorder, relative standard deviations were 5.2 % and 4.3 % for TTA and MBT, respectively.

These same sample aliquots also were used to evaluate the accuracy of the method. Results from the 10 separate analyses yielded concentrations of TTA (as 50 % sodium salt solution) that ranged from 2.16 mg/mL to 2.45 mg/mL (avg. 2.31 mg/mL vs. 2.30 mg/mL added). Concentrations of MBT (as 50 % sodium salt solution) ranged from 5.3 mg/mL to 5.8 mg/mL (avg. 5.6 mg/mL vs. 5.8 mg/mL added).

To evaluate the applicability of this method, several fresh and used engine coolant samples were processed using this procedure. In addition, recovery studies were performed by adding aliquots of standard solutions to each sample. Results are presented in Table 1 (for fresh) and 2 (for used). In the fresh formulations, recoveries ranged from 95.4 to 100.0 % (avg. 96.9 %) for TTA and from 100 to 106.0 (avg. 103 %) for MBT. For the used engine coolants, recoveries

TABLE 1. Results from Analyses of Typical Fresh Engine Coolants and Recoveries from Spiked Samples

	Found, mg/mL[a]		Spiked Sample Recoveries, mg/mL[a]			
			TTA		MBT	
Sample	TTA	MBT	Expected[b]	Found	Expected[b]	Found
1	1.78	< 0.1	2.97	2.85	5.0	5.3
2	2.14	< 0.1	3.33	3.24	5.0	5.3
3	1.84	< 0.1	3.03	2.89	5.0	5.1
4	< 0.05	5.7	2.38	2.29	15.7	16.4
5	2.22	5.8	4.60	4.50	15.8	15.9
6	2.20	5.7	4.58	4.58	15.7	15.8
7	2.31	4.8	4.69	4.49	14.8	14.8

[a] as 50 % solution of sodium salt.

[b] Expected amount is the amount initially found plus spike.

TABLE 2. Results from Analyses of Typical Used Engine Coolants and Recoveries from Spiked Samples

	Found, mg/mL[a]		Spiked Sample Recoveries, mg/mL[a]			
			TTA		MBT	
Sample	TTA	MBT	Expected[b]	Found	Expected[b]	Found
1 (4939 km)	0.87	< 0.1	1.46	1.49	2.5	2.6
2 (10300 km)	0.45	0.2	1.05	1.05	2.7	2.8
3 (19867 km)	0.17	< 0.1	0.76	0.79	2.5	2.5
4 (23294 km)	< 0.05	0.1	0.60	0.61	2.6	2.6
5 (unknown)	0.95	1.0	1.54	1.58	3.5	3.7
6 (72855 km)	0.36	< 0.1	0.96	0.93	2.5	2.6
7 (10849 km)	0.47	0.1	1.06	1.05	2.6	2.7
8 (12239 km)	0.30	0.2	0.90	0.90	2.7	2.6
9 (13538 km)	< 0.05	0.5	0.60	0.58	2.5	2.5
10 (43864 km)	0.79	2.0	1.38	1.36	4.5	4.6
11 (80467 km)	1.03	1.0	1.63	1.56	3.5	3.5

[a] as 50 % solution of sodium salt.

[b] Expected amount is the amount initially found plus spike.

ranged from 95.7 to 103.9 % (avg. 99.8 %) for TTA and from 96 to 106 % (avg. 102 %) for MBT.

If required, this method could be extended to accommodate lower concentrations of TTA and MBT by using larger sample aliquots or by increasing detector sensitivity. However, the sensitivity of this technique has been shown to be adequate to determine TTA and MBT in commercial ethylene glycol-based engine coolant formulations, both fresh and used.

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