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ANALYSIS OF METAL DEACTIVATORS IN LUBRICATING OILS

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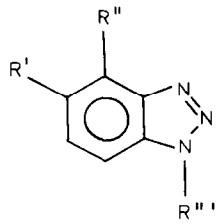
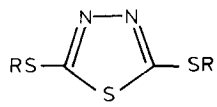
SUMMARY

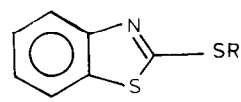
A rapid high-performance liquid chromatographic analysis is described for selected metal deactivators typically observed in fully formulated lubricating oils.

INTRODUCTION

Increasing equipment design sophistication and performance requirements place ever more severe demands on lubricants. Satisfactory lubricant performance is, in many instances, a direct result of the additive package blended with the base oil lubricant. Amos and Albaugh[1] have comprehensively reviewed the general classes of chemicals that typically compose an additive package. Among these components are corrosion and oxidation inhibitors. The term "metal deactivator" is often used in place of corrosion inhibitor; and benzotriazoles (I), mercaptothiadiazoles (II) and mercaptobenzothiazoles (III) are typical chemicals which fill the metal deactivator role in additive packages.







$R' = H, CH_3$
$R'' = H, CH_3$
$R''' = H, CH_2NR_2$

(I) (II) (III)

This paper reports a rapid high-performance liquid chromatographic (HPLC) separation technique for selected metal deactivators from a fully formulated lubricating oil matrix.

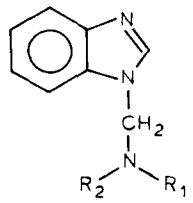
EXPERIMENTAL

Reagents

All chromatographic solvents were supplied by Burdick & Jackson Labs. Benzotriazole, 6-methylbenzotriazole, 5,6-dimethyl-1H-benzotriazole, and 2-mercaptobenzothiazole were obtained from Aldrich. The 7-methylbenzotriazole was isolated from a commercial mixture of metal deactivators by repetitive injections using an analytical column, then characterized by Fourier-transform-infrared, mass and ^{13}C nuclear magnetic resonance spectrometry.

Other commercial additives, N,N-dioctadecylamino-N-methylbenzotriazole (DAMB) and 2,5-bis(1,1,3,3-tetramethyldisulfhydryl)-1,3,4-thiadiazole (BTDT), were obtained and characterized in the same manner. The structure of (IV) was obtained by first separating the additive from diluting oil by a normal-phase preparative separation using a Waters Prep-Pak® amino-bonded phase column. The oil was eluted with *n*-hexane, then the DAMB with methylene chloride.

(DAMB)



$R_1 = R_2$ = Octadecyl

(IV)

The antioxidants selected as typical components of an additive package, N-phenyl-1-naphthylamine (Aldrich), 2,6-di-*tert.*-butyl-4-methylphenol (Aldrich), 4,4′-tetramethyldiaminodiphenylmethane (American Cyanamide), and 4,4′-methylenebis[2,6-di-*tert.*-butyl-4-methylphenol] (Fisher Scientific) were used as received.

Apparatus

All UV spectra were obtained from a Cary Model 14 recording spectrophotometer with the metal deactivators dissolved in acetonitrile or isopropanol–acetonitrile mixtures.

Samples were autoinjected using a Spectra-Physics Model SP8010 autosampler. A Spectra-Physics SP8000 liquid chromatograph fitted with a 25-μl sample loop and a commercially packed amino-bonded phase column (25 cm × 4.6 mm, Spheresorb S5NH, Regis Chemical) resolved each sample mixture. All separations were carried out at 2 ml/min flow-rate. A Schoeffel Model 770 variable-wavelength detector tuned to 254 or 325 nm supplied signal output to the SP8000 data system for peak area determination. Benzotriazole derivatives were separated using a mobile phase of acetic acid–isopropanol–hexane (0.1:10:89.9, v/v/v). Thiadiazole derivatives were

TABLE I

COMPOSITION OF SAMPLE LUBRICATING OILS

Component	*Matrix A*	*Matrix B*
Viscosity index improver	Olefin homopolymer	Polyalkylmethacrylate
Oxidation inhibitors	2,6-Di-*tert.*-butyl-4-methylphenol	4,4'-Tetramethyldiamino-diphenylmethane
	N-Phenyl-1-naphthylamine	4,4'-Methylenebis(2,6-di-*tert.*-butylphenol)
Extreme pressure additive	Polysulfurized paraffin	Polysulfurized paraffin
Dispersant	–	Polyamide
Foam inhibitor	Polysiloxane	Polysiloxane
Base oil	Commercial blend	Commercial blend

chromatographed with isopropanol–ethylene chloride-hexane (0.02:1.75:98.23, v/v/v).

Sample preparation

Two sample lubricating oils (Matrix A and Matrix B) were prepared using typical concentrations of the additive package components shown in Table I.

Stock standard solutions of each metal deactivator studied were prepared by dissolving a weighed amount of each substance in a suitable solvent. Weighed amounts of this stock solution were then added to a weighed amount of the lubricating oil matrix under study. Prior to injection, the fully formulated lubricant matrix was diluted 1:1 (w/w) with isooctane to reduce the sample viscosity.

RESULTS AND DISCUSSION

Benzotriazole and its derivatives

The highly polar nature of benzotriazole and its derivatives in comparison with the non-polar hydrocarbon lubricant suggests a normal-phase chromatographic approach would be productive. An amino-bonded phase column was selected over a silica material because of the resiliency of the bonded phase material compared to raw silica. Since benzotriazole and its derivatives also posses ultraviolet (UV) chromophores of significant magnitude (Fig. 1), monitoring column effluent in the UV region gives excellent sensitivity for detection purposes. Although the hindered phenol and amine oxidation inhibitors selected for this study have similar spectral characteristics, two factors prevent interferences with the benzotriazole derivatives. First, reasonable elution time for the benzotriazoles requires such a strong mobile phase that the oxidation inhibitors are unretained by the column (presumably because of the sterically hindered position of the polar group in the molecule). Second, the UV spectrum of many of these oxidation inhibitors possesses a minimum near 250 nm. Even if a worst-case situation is assumed where no chromatographic resolution between metal deactivator and oxidation inhibitor is obtainable, interferences can be minimized by detecting the metal deactivator selectively at 254 nm. There were no spectral/chromatographic interferences between the compounds selected for this study; but for other combinations, selective detection may be an important consideration.

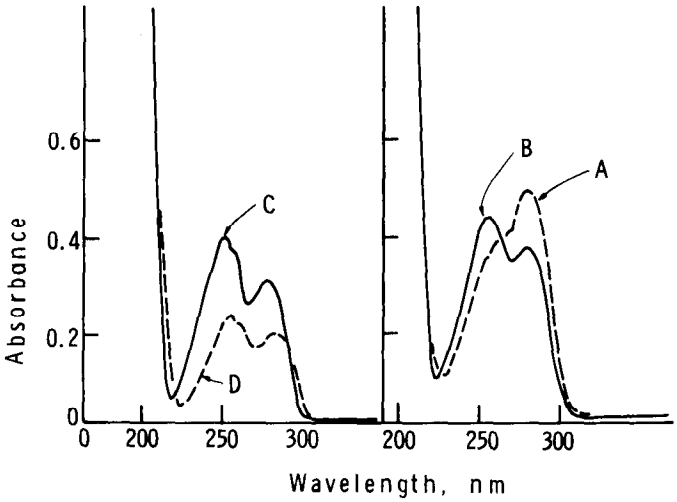


Fig. 1. UV spectra of (A) DAMB (0.3676 g/l); (B) 6-methylbenzotriazole (0.1232 g/l); (C) benzotriazole (0.401 g/l); (D) 5,6-dimethyl-1H-benzotriazole (0.0652 g/l). All spectra recorded in 0.10-cm cell. (A) recorded in *n*-hexane; all others in acetonitrile.

TABLE II

ANALYSIS OF LUBRICATING OIL MATRIX CONTAINING SELECTED METAL DEACTIVATORS

Replicates = 6; UV detection at 254 nm (0.4 absorbance units full scale). R.S.D. = Relative standard deviation.

Sample	*Component*	*Concentration (ppm)*		*R.S.D. (%)*
		Added	*Found*	
1	7-Methylbenzotriazole	3.3	2.3	5.9
	6-Methylbenzotriazole	3.6	3.1	11.1
	Benzotriazole	6.7	4.0	11.6
2	7-Methylbenzotriazole	24.3	23.7	3.9
	6-Methylbenzotriazole	26.3	25.8	4.1
	Benzotriazole	48.4	47.3	2.7
3	7-Methylbenzotriazole	40.4	40.8	1.2
	6-Methylbenzotriazole	44.5	44.8	1.7
	Benzotriazole	81.3	83.0	1.0
4	7-Methylbenzotriazole	49.6	50.0	0.4
	6-Methylbenzotriazole	54.6	54.6	0.3
	Benzotriazole	99.9	100.4	1.6
5	7-Methylbenzotriazole	68.6	70.5	1.4
	6-Methylbenzotriazole	75.9	77.7	1.7
	Benzotriazole	138.8	143	0.7
6	7-Methylbenzotriazole	140	138.9	1.1
	6-Methylbenzotriazole	154.5	153.6	1.8
	Benzotriazole	284.2	281.6	1.3

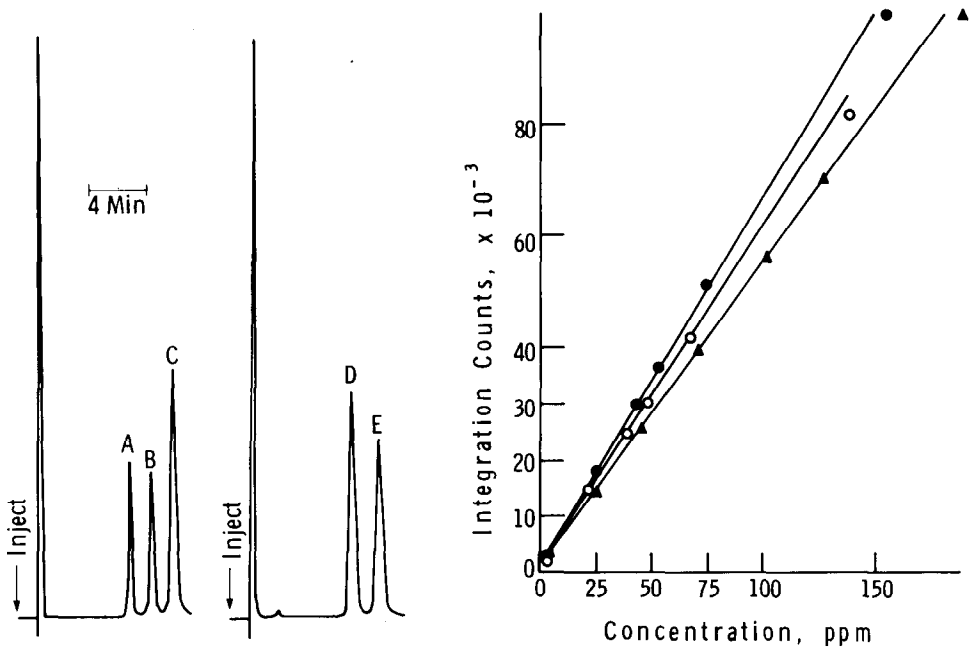


Fig. 2. Separation of (A) 7-methylbenzotriazole, (B) 6-methylbenzotriazole, (C) benzotriazole, (D) 5,6-dimethyl-1H-benzotriazole and (E) DAMB. Chromatographic conditions are listed in Experimental section.

Fig. 3. Response curves for 6-methylbenzotriazole (●), 7-methylbenzotriazole (○), and 5,6-dimethyl-1H-benzotriazole (▲). UV detector, 254 nm (0.4 absorbance units full scale); 1 μV/sec = 1 integration count.

Table II compares the amounts found against those added for 7-methylbenzotriazole, 6-methylbenzotriazole and benzotriazole itself in Matrix A and Matrix B lubricants. Sample 1 of this series shows rather poor recovery, reflecting the approach to the limits of detection for these compounds with this approach. Fig. 2 shows a typical chromatogram observed for these separations. No significant difference was noted between analytical results for the two lubricant matrices; hence, the results were combined for precision evaluation. Fig. 3 shows the response curve for 7-methylbenzotriazole, 6-methylbenzotriazole and 4,5-dimethylbenzotriazole. Table III lists the amounts found against amounts added for 4,5-dimethylbenzotriazole and DAMB. Again, no significant difference existed between the lubricant matrices; thus results were combined. Fig. 4 is the response curve generated with DAMB and benzotriazole itself.

Mercaptothiadiazoles and mercaptobenzothiadiazoles

These compounds are quite difficult to chromatograph. The column retention is exceptionally sensitive to even small concentration changes in the mobile-phase polar modifier. In addition, these compounds tend to "tail" badly during elution, apparently due to the sulfhydryl moiety in the molecule. The metal deactivator 2,5-bis(1,1,3,3-tetramethyldisulfhydryl)-1,3,4-thiadiazole (BTDT; V) can be chromatographed successfully, apparently because the disulfide linkage eliminates the highly basic sulfhydryl groups. Fig. 5 shows the UV spectrum of BTDT.

TABLE III

ANALYSIS OF LUBRICATING OIL MATRIX CONTAINING SELECTED METAL DEACTIVATORS

UV detection at 254 nm (0.4 absorbance units full scale); replicates = 6. DAMB = (N,N-dioctadecyl)amino-N-methylbenzotriazole; R.S.D. = Relative standard deviation.

Sample	*Components*	*Concentration (ppm)*		*R.S.D. (%)*
		Added	*Found*	
1	5,6-Dimethyl-1H-benzotriazole	5.3	3.9	11.7
	DAMB	17.0	14.7	9.5
2	5,6-Dimethyl-1H-benzotriazole	25.2	25.4	1.9
	DAMB	80.1	78.7	3.5
3	5,6-Dimethyl-1H-benzotriazole	47.2	47.0	1.5
	DAMB	143.6	143.8	6.6
4	5,6-Dimethyl-1H-benzotriazole	71.2	71.3	2.5
	DAMB	220	216	5.2
5	5,6-Dimethyl-1H-benzotriazole	102.1	104.1	0.66
	DAMB	318.8	326.5	1.14
6	5,6-Dimethyl-1H-benzotriazole	128	129.6	0.39
	DAMB	400.7	408.1	0.77
7	5,6-Dimethyl-1H-benzotriazole	189	186.9	0.29
	DAMB	600.2	592.5	1.74

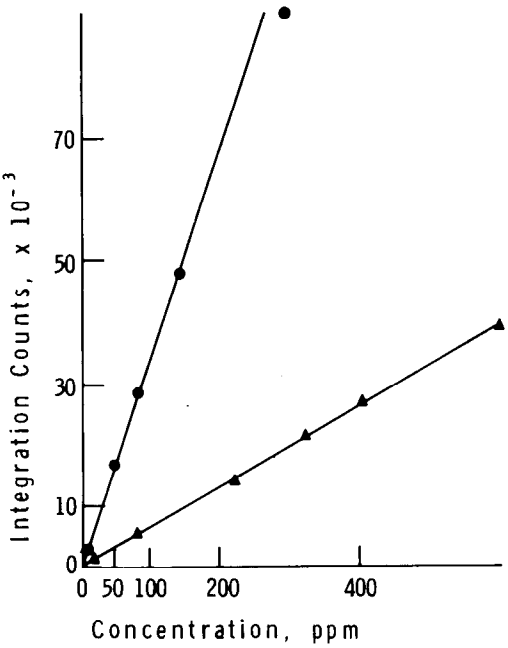
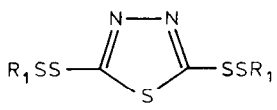
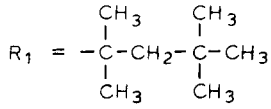


Fig. 4. Response curves for benzotriazole (●) and DAMB (▲). UV detector, 254 nm (0.4 absorbance units full scale); 1 μV/sec = 1 integration count.

(BTDT)





(V)

While no significant "tailing" is seen with BTDT, its column retention is very sensitive to the amount of polar modifier (isopropanol) in the mobile phase. Fig. 6 details the retention behavior of BTDT and N-phenyl-1-naphthylamine with small changes in the isopropanol concentration. Note also the change in elution order with a small change in isopropanol concentration. In addition, a much weaker mobile phase (relative to the benzotriazoles) is required to achieve column retention of BTDT. This complicates the separation, because components previously unretained by the column can now interfere. Monitoring at 325 nm can eliminate a majority of these spectral interferences; however, N-phenyl-1-naphthylamine and 4,4′-tetramethyldiaminodiphenylmethane possess some absorption at 325 nm (see Fig. 7); and these compounds must be resolved chromatographically. By very careful adjustment of isopropanol in the mobile phase, BTDT can be separated and quantified. Table IV lists recoveries of BTDT in the presence of varying amounts of N-phenyl-1-naphthylamine and 4,4′-tetramethyldiaminodiphenylmethane. At amine:thiadiazole

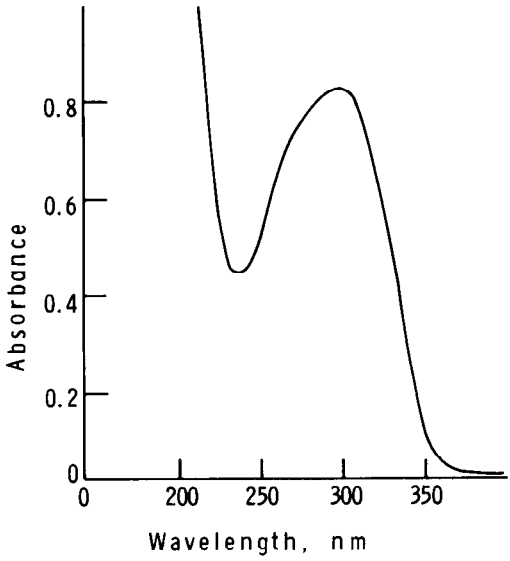


Fig. 5. UV spectrum of BTDT. Solvent, *n*-hexane (0.5008 g/l), 1.0-cm cell.

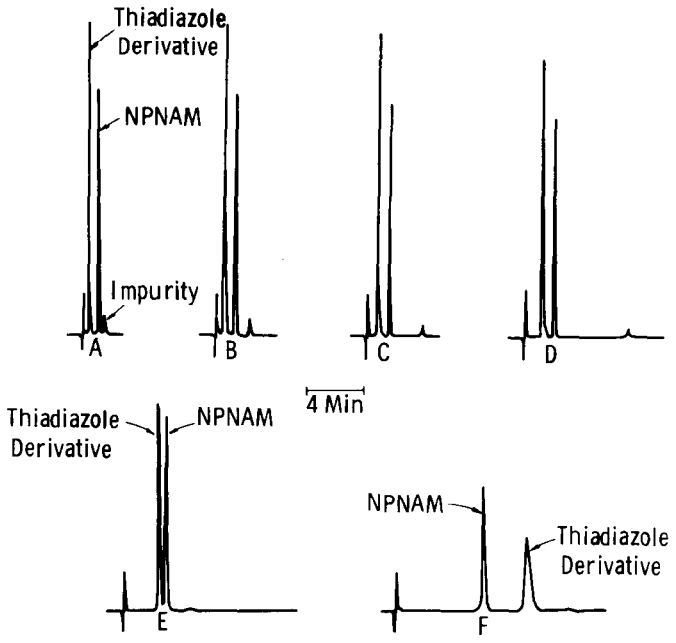


Fig. 6. The effect of mobile phase composition on the separation of thiadiazole derivative, BTDT and N-phenyl-1-naphthylamine (NPNAM); (A) 0.40% isopropanol, 1.75% ethylene chloride, 97.85% *n*-hexane; (B) 0.32% isopropanol; (C) 0.25% isopropanol; (D) 0.17% isopropanol; (E) 0.10% isopropanol; (F) 0.02% isopropanol, 1.75% ethylene chloride, 98.23% *n*-hexane.

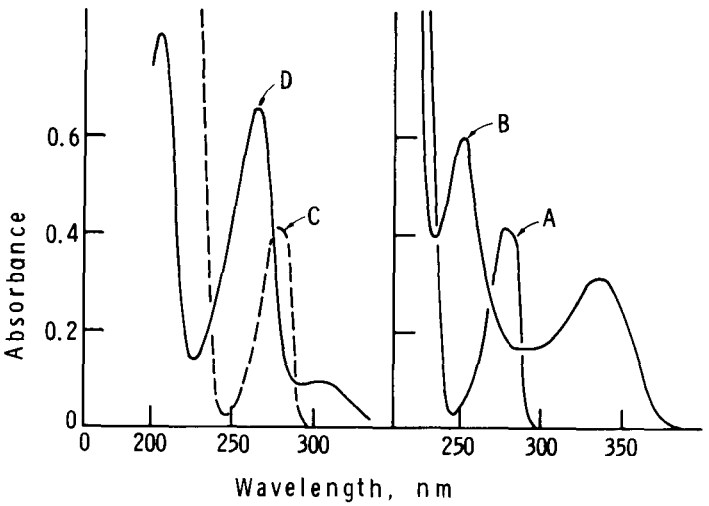


Fig. 7. UV spectra of (A) 4,4′-methylenebis(2,6-di-*tert.*-butylphenol) (0.0057 g/l); (B) N-phenyl-1-naphthylamine (0.0680 g/l); (C) 2,6-di-*tert.*-butyl-4-methylphenol (0.481 g/l); (D) 4,4′-tetramethylene-diaminodiphenylmethane (0.0540 g/l). All spectra recorded in 0.1-cm cell.

TABLE IV

ANALYSIS FOR BTDT IN THE PRESENCE OF SELECTED ANTIOXIDANT ADDITIVES

Replicates = 6; UV detection at 325 nm. R.S.D. = Relative standard deviation.

4,4'-Tetramethyldiamino-diphenylmethane (ppm)	*N-Phenyl-1-naphthylamine (ppm)*	*Metal deactivator (ppm)*		*R.S.D. (%)*
		Added	*Found*	
293	–	892	884	0.88
1369	–	978	966	1.3
1459	–	1012	1008	0.95
659	–	1048	1048	1.6
–	183	870	883	0.9
–	416	978.1	998	1.5
–	777	1062	1052	1.7

ratios of 0.2:1, recovery of the thiadiazole from the compounded oil is in error by less than 2%. Thus, even these difficult-to-separate compounds can be quantitatively determined with this method.

Further work is in progress aimed at development of separations for mercaptobenzothiadiazole and dimercaptothiadiazoles from other fully formulated lubricants.

ACKNOWLEDGEMENTS

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