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Size-exclusion chromatography method for characterizing low-molecular-mass antioxidant lubricant additives

Susan V. Greene*, Vincent J. Gatto

Ethyl Petroleum Additives, Inc., P.O. Box 2158, 500 Spring Street, Richmond, VA 23218-2158, USA

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Abstract

The use of size-exclusion chromatography to characterize complex mixtures of low-molecular-mass additives is presented. These antioxidant lubricant additives are oligomers derived from more than one monomer unit and have a molecular mass generally in the range 150–1000. The technique separates these mixtures into molecular mass regions, which produce a fingerprint characteristic of the product. The fingerprints are correlated with molecular structure using standards known to be present in the mixtures. The method can be used as a quality control tool and a research tool for product characterization.

Keywords: Lubricants; Antioxidants; Polymers; Phenolic compounds; Amines

1. Introduction

The use of antioxidants to stabilize organic materials is a common and well documented practice [1]. In the lubricant industry, methylene bridged hindered phenolic antioxidants and alkylated diphenylamine antioxidants have demonstrated performance over many years. A substantial amount of research has also been done on the development and application of sulfur bridged hindered phenolic antioxidants [2,3]. These antioxidants are prepared by alkylation reactions, resulting in the formation of complex product mixtures. For the phenolic antioxidants these mixtures are composed of methylene or sulfur bridged hindered phenolic oligomers and a variety of hindered phenolic isomers [3,4]. For the alkylated diphenylamines these mixtures are composed of mono- and dialkylated diphenylamines and various structural isomers [5,6]. Methods of analyzing these mixtures include gas chromatography (GC) [6] and high-performance liquid chromatography (HPLC) [7]. For multicomponent mixtures these two kinds of analytical methods produce complex chromatograms with little structural information about the individual components of the mixture. Proton nuclear magnetic resonance (NMR) has been used to analyze mixtures of sulfur bridged hindered phenolic antioxidants but this method is limited to very simple product mixtures [8]. GC is limited to relatively volatile additive mixtures. High-molecular-mass antioxidant oligomers or thermally unstable antioxidants, cannot be analyzed by GC.

Size-exclusion chromatography (SEC), more commonly called gel permeation chromatography (GPC), has been used extensively to characterize high-molecular-mass polymers and oligomers of various polymer classes [9]. There have also been reports on the use of SEC to identify low-molecular-mass

*Corresponding author. Fax: +1-804-788-6244.

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compounds including additives in polymers [10–15]. The compounds and additives in these studies were of high purity and identified based on their SEC retention times. One report has shown the use of SEC to characterize low-molecular-mass oligomers produced by the condensation of nonylphenol with formaldehyde, or the polymerization of 2,2,4-trimethyl-1,2-dihydroquinoline [16].

This paper extends the application of SEC to characterize more complex mixtures of low-molecular-mass additives such as oligomers derived from more than one monomer unit, and specifically lubricant antioxidants. It presents a new use and application of SEC that allows one to abstract structural and compositional information about complex additive mixtures. The method simplifies characterization of these additives since components of the mixtures are grouped in the chromatogram based on molecular mass or hydrodynamic volume, and not boiling point as with GC, or polarity as with HPLC. The method is used to analyze the methylene bridged hindered phenols and alkylated diphenylamines mentioned above, as well as some experimental sulfurized hindered phenolic antioxidants that are currently under development in the lubricant industry [3]. The application of this method as a product development tool and a quality control tool is demonstrated.

2. Experimental

2.1. Materials

2.1.1. Commercial and developmental lubricant antioxidant products

The methylene bridged *tert*.-butylphenol antioxidants (products A and B), the developmental sulfur bridged *tert*.-butylphenol antioxidants (products C and D) and the alkylated diphenylamine antioxidant (product E) were obtained from Ethyl Petroleum Additives (Richmond, VA, USA). The alkylated diphenylamine antioxidants (products F, G and I) were obtained from Uniroyal Chemical Co. (Middlebury, CT, USA). The alkylated diphenylamine antioxidants (products H and J) were obtained from Ciba Specialty Chemicals (Hawthorne, NY, USA).

2.1.2. SEC standards

4,4′-Methylenebis(2,6-di-*tert*.-butylphenol) (standard A), 2,6-di-*tert*.-butylphenol (DTBP) (standard C) and 4,4′-thiobis(2,6-di-*tert*.-butylphenol) (standard E) were obtained from Ethyl Petroleum Additives. 2,4,6-Tri-*tert*.-butylphenol (standard B), *o*-*tert*.-butylphenol (standard D) and diphenylamine (standard M) were obtain from Aldrich (Milwaukee, WI, USA). Dioctyldiphenylamine (standard F), butyloctyldiphenylamine (standard G), dibutyldiphenylamine (standard H), distyryldiphenylamine (standard I), monooctyldiphenylamine (standard J), monobutyldiphenylamine (standard K) and monostyryldiphenylamine (standard L) were obtained from BFGoodrich (Cleveland, OH, USA).

2.1.3. Chromatography

HPLC-grade tetrahydrofuran (THF), unstabilized, was purchased from Fisher (Fair Lawn, NJ, USA). Nylon syringe filters, with a pore size of 0.45 μm and 13 mm diameter, were from Rainin (Woburn, MA, USA).

2.2. Chromatographic system and conditions for assay

The Waters (Waters, Milford, MA, USA) SEC chromatographic system included a 600E system controller and solvent delivery module, a 410 differential refractive index (DRI) detector, a 717 autosampler and Millennium Software, version 2.15. The analytical columns (Polymer Labs., Amherst, MA, USA) consisted of a bank of three PLgel polystyrene–divinylbenzene SEC columns containing 5 μm particles of 100 Å porosity. All columns were 300×7.5 mm and were maintained at ambient temperature. Filtered samples and standards were analyzed by injecting a 20 μl solution into the SEC system. The flow-rate was 1 ml/min with the DRI detector sensitivity set at 64. Molecular mass regions from the chromatograms were reported as percentage areas of a sample.

2.3. Sample and standard preparation

Samples were prepared at a nominal concentration of 5 mg/ml in THF, and filtered into an autosampler vial using a 0.45-μm nylon syringe filter and a glass

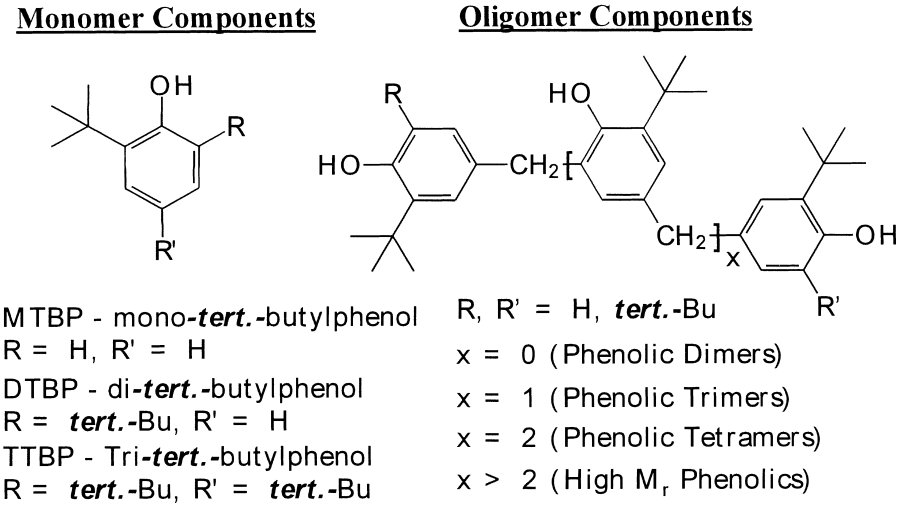

Fig. 1. Chemical structures present in methylene bridged *tert*.-butylphenolic antioxidants.

syringe. Standards were prepared in a similar fashion at a nominal concentration of 1 mg/ml. Standards were used to identify the molecular mass region where that chemistry eluted from the column.

3. Results and discussion

3.1. Methylene bridged hindered tert.-butylphenolic antioxidants

The various molecular structures contained in the methylene bridged *tert*.-butylphenolic antioxidants (products A and B) are shown in Fig. 1. The complexity of the methylene bridged hindered *tert*.-butylphenol (MTBP) products is attributed to their degree of oligomerization, or *x* value in Fig. 1, and the presence of MTBP and DTBP derived monomer units within the oligomers. The presence of two monomer units results in oligomer components where R and R′ may be hydrogen (H) or *tert*.-butyl (*tert*.-Bu).

Fig. 2 shows the SEC chromatogram obtained from analysis of product A. It demonstrates the resolution of this SEC method, with separation of TTBP monomer from the higher-molecular-mass

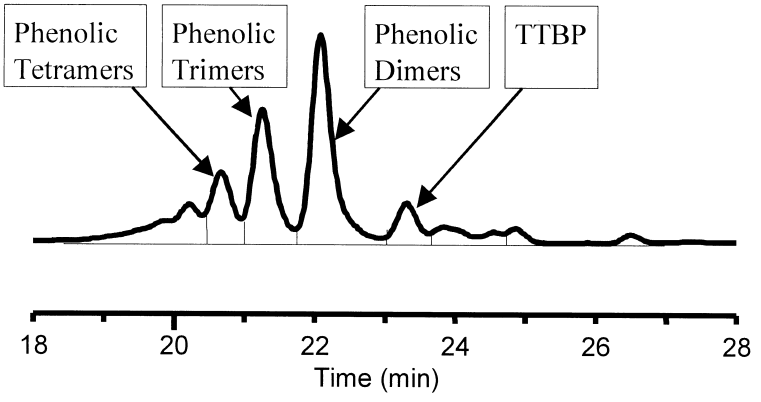

Fig. 2. SEC chromatogram of a methylene bridged *tert*.-butylphenolic antioxidant – product A. The *y*-axis units from the DRI detector are in mV with a maximum response of 40 mV.

oligomers. The method also resolves the various dimers, trimers and tetramers present in the oligomer portion of the product. The unlabeled peaks with retention times less than about 20.5 min correspond to high-molecular-mass phenolic oligomers, while the unlabeled peaks with retention times greater than about 23.5 min correspond to monomer components and low-molecular-mass impurities. Assignment of TTBP and the oligomer components in this chromatogram is based on comparison with the retention times obtained for the known standards presented in Table 1, combined with predictions based on the linear relationship between retention time and log (molecular mass). A discussion of this linear relationship is given below.

Table 1 provides the peak retention times, with appropriate area percentages, obtained from chromatograms of products A and B. The retention times of the pure standard materials are also included in the table. Standards B, C and D were selected because they are the monomers used in the preparation of the products. Standard A was selected because it represents an expected component produced in the synthesis of the products. Each column in Table 1 corresponds to one peak of a complete SEC chromatogram. The top row of data presents the retention time ranges for all the peaks in the chromatogram. Below the retention times are the molecular mass ranges corresponding to specific peak retention times. Below the molecular mass ranges are the SEC region classifications based on the molecular types present in products A and B, and standards A–D.

Table 1 shows that certain peak retention times found in products A and B correspond to peak retention times obtained for the purified standards. It is important to note that the standards are pure compounds with precise molecular masses that fall within defined peak retention time ranges. Products A and B, on the other hand, are complex mixtures and contain a number of structurally different molecules within a given peak.

The results in Table 1 identify a number of key structural and compositional variations between products A and B. These variations are critical when interpreting the physical differences observed between products A and B. A comparison among the physical properties of products A and B, and standard A, is shown in Table 2. Product B has greater oil solubility and is less crystalline than product A. Standard A is crystalline with a high melting point and poor oil solubility. Therefore, differences in the quantity of standard A found in products A and B are the likely causes of these physical property variations. It is also likely that the higher monomer content, especially DTBP, found in product B is

Table 1
Low-molecular-mass SEC analysis of methylene bridged hindered *tert.*-butylphenolic antioxidants and standards (single injection determinations)[a, b]

SEC retention time range (min)									
	20.0–20.3	20.3–20.5	20.8–20.9	21.4–21.5	22.0–22.4	23.4–23.6	24.1	24.3–24.6	25.0–25.2
Molecular mass range (calculated)									
	966–1078	802–915	639–751	476–588	312–425	262		206	150
SEC region classification									
	High-M_r phenolics	High-M_r phenolics	Phenolic tetramers	Phenolic trimers	Phenolic dimers	TTBP		DTBP	MTBP
SEC standard identification (standard represents >99.0% area)									
Standard identity					Standard A	Standard B		Standard C	Standard D
Methylene bridged phenols (% area of sample)									
Product A	4.8	6.0	12.1	24.3	40.7	6.4	1.0	1.9	2.7
Product B	18.4	10.5	16.1	13.8	20.4	1.9		16.4	2.5

[a] See Experimental for description of products and standards.

[b] Molecular mass (M_r) ranges calculated from all chemical structures in Fig. 1. Calculations for oligomer components based on all combinations, where R=H and *tert.*-Bu, R′=H and *tert.*-Bu, and x=0, 1, 2, 3, 4.

Table 2
Properties of bridged hindered phenolic antioxidant products and standards

Property	Standard A	Product A	Product B	Standard E	Product C	Product D
Antioxidant class						
	Methylene bridged hindered phenolic	Methylene bridged hindered phenolic	Methylene bridged hindered phenolic	Sulfur bridged hindered phenolic	Sulfur bridged hindered phenolic	Sulfur bridged hindered phenolic
Appearance at room temperature						
	Yellow solid m.p.=155–156°C	Semi-crystalline glass	High-viscosity liquid	Yellow solid m.p.=138–140°C	High-viscosity liquid	Semi-crystalline liquid
Solubility in baseoil						
	Very low	Low	High	Very low	High	Low
TGA mass loss temperature ramp (°C, under nitrogen)						
10%	212	139	128	228	114	123
50%	251	260	313	272	246	250
90%	269	396	550	293	306	291

contributing to its improved oil solubility. The monomers have much higher solubility in oil than the oligomers prepared from them.

Products A and B also differ in their thermogravimetric analysis (TGA) volatility profiles. This is attributed to differences in monomer content and high-molecular-mass phenolic content between the two products.

The linear relationship between peak retention time and log (molecular mass) for the combined products A and B, and standards A–D, is shown in the methylene bridged *tert*.-butylphenols linear regression analysis found in Table 3. This model is what allows one to predict the structures of the higher molecular mass components found in products A and B ($x>1$).

3.2. Sulfur bridged hindered tert.-butylphenolic antioxidants

The various molecular structures contained in the sulfur bridged *tert*.-butylphenolic antioxidants (products C and D) are shown in Fig. 3. The composition of these materials is similar to that of the methylene bridged hindered phenolic antioxidants, but with one additional level of complexity. The sulfurized materials possess bridges with varying numbers of sulfur. This is indicated by $y=1$, 2, 3, 4, or higher. It has been shown that the number of sulfurs present in a sulfurized hindered *tert*.-butylphenol bridge depends on the method of preparation [3].

Fig. 4 shows the SEC chromatogram obtained from analysis of product C. The SEC method

Table 3
Regression analysis for component molecular mass model: log (molecular mass)=m(retention time)+b

Model parameters	Methylene bridged *tert*.-butylphenols	Sulfur bridged *tert*.-butylphenols	Alkylated diphenylamines
Standards used (No.)	4	4	8
Products used (No.)	2	2	5
Total data points	35	30	43
Slope, m	−0.374	−0.371	−0.226
Standard error of slope	0.0113	0.00893	0.0117
Intercept, b	14.3	14.3	11
Standard error of intercept	0.244	0.2	0.278
Correlation coefficient	−0.984	−0.992	−0.949
R^2	0.968	0.984	0.901
Standard error of estimate	0.107	0.0682	0.0912

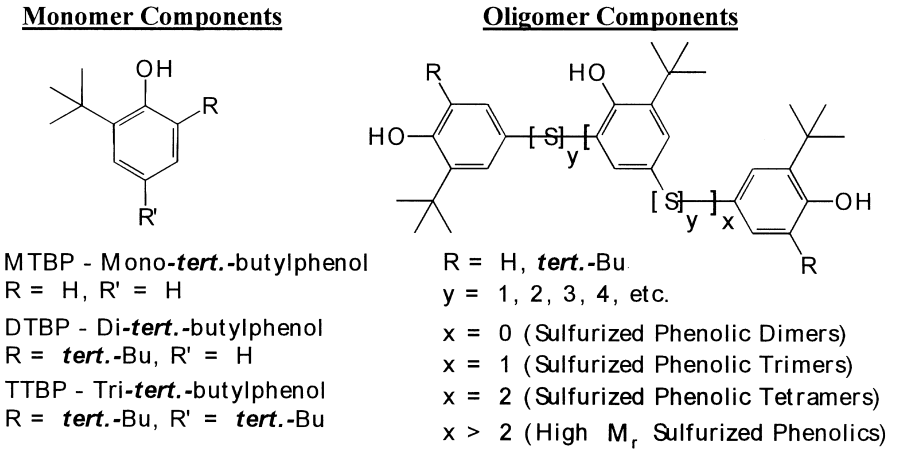

Fig. 3. Chemical structures present in sulfur bridged *tert.*-butylphenolic antioxidants.

effectively resolves the TTBP monomer from the higher-molecular-mass oligomers. MTBP and DTBP are more easily detected in this product and are clearly resolved from each other and from TTBP. The method also resolves the various oligomers present in the product. A comparison between the SEC chromatogram of methylene bridged product A (Fig. 2) and sulfur bridged product C (Fig. 4) shows that the sulfurized product contains fewer high-molecular-mass components. However, in the case of the sulfurized products, many more components are present within the dimer, trimer and tetramer peaks of the SEC chromatogram. This is because the sulfur bridges themselves can vary in the number of sulfurs present. Bridges containing 1, 2, 3 or more sulfurs are possible. The methylene bridging groups can only produce one type of bridge.

Table 4 presents the SEC results for products C and D along with standards B, C, D and E. Sulfurized hindered phenolic products C and D are very similar in their various monomer contents but are quite different in their distribution of oligomers. Both products have approximately the same percentages of total oligomers, which is defined as the sum of dimers, trimers and tetramers. Product C, however, is substantially higher in trimer and tetra-

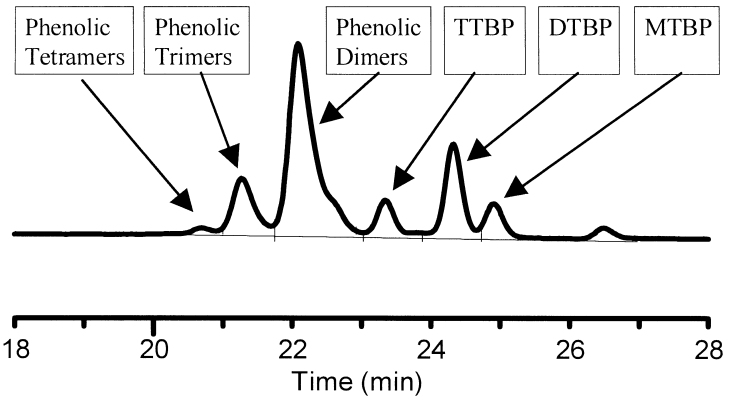

Fig. 4. SEC chromatogram of a sulfur bridged *tert.*-butylphenolic antioxidant – product C. The *y*-axis units from the DRI detector are in mV with a maximum response of 40 mV.

Table 4
Low-molecular-mass SEC analysis of sulfur bridged hindered *tert*.-butylphenolic antioxidants and standards (single injection determinations)[a, b]

SEC retention time range (min)	20.7	21.3	22.1–22.4	23.4–23.6	24.3–24.6	24.9–25.2
Molecular mass range (calculated)	749–838	568–656	387–475	262	206	150
SEC region classification	Phenolic tetramers	Phenolic trimers	Phenolic dimers	TTBP	DTBP	MTBP
SEC standard identification (standard represents >99.0% area)						
Standard identity			Standard E	Standard B	Standard C	Standard D
Sulfurized phenols (% area of sample)						
Product C	1.7	13.6	53.5	7.3	17.3	6.6
Product D		2.9	70.2	5.6	16.7	4.6

[a] See Experimental for description of products and standards.
[b] Molecular mass (M_r) ranges calculated from all chemical structures in Fig. 3. Calculations for oligomer components based on all combinations, where R=H and *tert*.-Bu, $x=0$, 1, 2 and $y=1$, 2.

mer content. As seen in Table 2, these structural and compositional differences translate to differences in physical properties and volatility.

The linear relationship between peak retention time and log (molecular mass) for the combined products C and D, and standards B–E, is shown in the sulfur bridged *tert*.-butylphenols linear regression analysis found in Table 3. Note that the model for predicting methylene bridged *tert*.-butylphenol molecular mass and sulfur bridged *tert*.-butylphenol molecular mass are virtually identical. This shows the broad application of this SEC technique for characterizing bridged hindered phenolics in general. The technique should be applicable to other classes of hindered phenols such as *sec*.-butyl, isopropyl, *tert*.-amyl and nonyl, as well as other types of bridging groups such as ethylidene, butylidene and phosphorus. Repeatability of the method is demonstrated by the analysis of eight different laboratory prepared samples of product C. The standard error on each retention time for the eight samples ranged from 0.0027 min to 0.0076 min. The standard error on the dimer, trimer and tetramer area percentages were 0.076%, 0.27% and 0.55%, respectively. Such repeatability on both retention times and areas offers advantages over HPLC methods for product development in research and development and quality control in production. In addition, over a three-year period several hundred samples were analyzed using the same set of SEC columns with no significant drift in retention time.

3.3. Alkylated diphenylamine antioxidants

The chemical structures present in the alkylated diphenylamine antioxidants (products E–J) are shown in Fig. 5. This chemistry is very different from the hindered phenol oligomer chemistry discussed above. The diphenylamine products are composed primarily of monoalkylateddiphenylamines (MADPA) and dialkylateddiphenylamines (DADPA). Products E and F contain octyl and styryl groups in various combinations and proportions. Products G and H contain octyl and butyl groups, while products I and J contain only nonyl groups. The presence of structural isomers in all of these products adds to their complexity.

Fig. 6 shows the SEC chromatogram obtained from analysis of product E. Analysis of all the diphenylamine products is provided in Table 5. Each peak in Fig. 6 has been identified using standards F–M listed in Table 5. Two standards, H (dibutyldiphenylamine) and I (distyryldiphenylamine), fall within the same retention time range. These two standards have very different molecular masses but elute at approximately the same time on the SEC

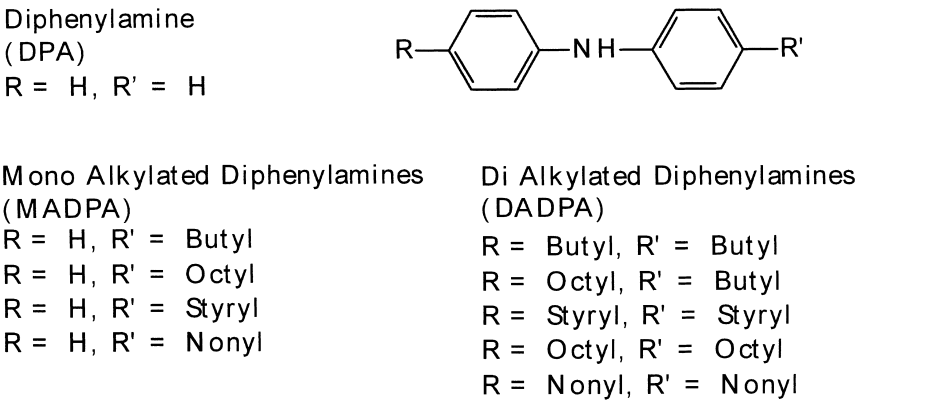

Fig. 5. Chemical structures present in alkylated diphenylamine antioxidants.

column. Standards were not available for butylstyryldiphenylamine or octylstyryldiphenylamine, so identifying the peaks containing these potential components was not possible. All other standards have retention times corresponding to one peak in Fig. 6 or one column in Table 5.

Table 5 shows some interesting results. First, the octylstyryl based products E and F all contain peaks in the retention time range corresponding to monobutyldiphenylamine (24.3 to 24.4 min). This shows that the octylstyryl based products contain some butyl alkylated product as well. Second, the nonyl based products I and J are compositionally quite different from the octylstyryl or octylbutyl materials. The nonyl products contain a much higher DADPA content. Understanding these composition differences can be of value when comparing the performance of these products in various lubricant applications.

The linear relationship between peak retention time and log(molecular mass), for the products E–J and standards F–M, is shown in the alkylated diphenylamine linear regression analysis found in Table 3. Note that the model for predicting alkylated diphenylamine molecular mass is quite different from that of the bridged *tert*.-butylphenols. Also, the R^2 value of the alkylated diphenylamine model is significantly lower than the R^2 value for the bridged

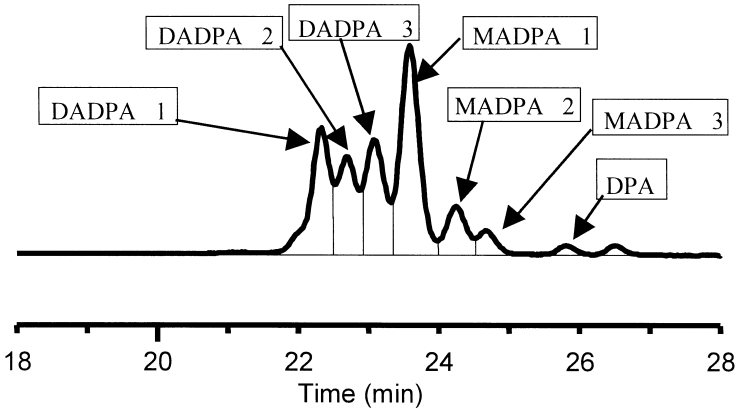

Fig. 6. SEC chromatogram of an alkylated diphenylamine antioxidant – product E. The *y*-axis units from the DRI detector are in mV with a maximum response of 40 mV.

Table 5
Low-molecular-mass SEC analysis of alkylated diphenylamine antioxidants and standards (single injection determinations)[a, b]

SEC retention time range (min)	21.1–21.3	21.8–21.9	22.3–22.4	22.7–22.8	23.1–23.4	23.6–23.7	24.3–24.4	24.8	25.8–26.1
Molecular mass range (calculated)			394–422	338	282–378	282–296	225	273	169
SEC region classification	?	?	DADPA 1	DADPA 2	DADPA 3	MADPA 1	MADPA 2	MADPA 3	DPA
SEC standard identification (standard represents >99.0% area)									
Standard identity			Standard F	Standard G	Standards H, I	Standard J	Standard K	Standard L	Standard M
Octylstyryldiphenylamines (% area of sample)									
Product E			20.5	15.3	17.3	34.8	7.3	3.6	1.2
Product F			21.6	8.6	16.1	39.7	8.8	3.9	1.3
Octylbutyldiphenylamines (% area of sample)									
Product G			12.9	35.6	18.2	14.1	17.9		1.4
Product H			23.1	30.5	6.3	25.1	14.1		1
Nonyldiphenylamines (% area of sample)									
Product I	0.9	7.5	68.1			21.4			1.7
Product J	0.9	1.9	73.6			22.5			

[a] See Experimental for description of products and standards.
[b] Molecular mass ranges calculated from all chemical structures in Fig. 5.

tert.-butylphenol models. The drastic difference in phenolic and diphenylamine chemistry may explain the differences seen in the slope and intercept in these models. These results show that significant differences in chemistry would require evaluating new standards to establish accurate models. New standards should always be identified and analyzed whenever new chemistry is being investigated.

4. Conclusions

Complex mixtures of lubricant additives, in this paper methylene bridged hindered phenols, sulfur bridged hindered phenols and alkylated diphenylamines, can be characterized using a low-molecular-mass SEC method. The technique can provide reasonable separations of product mixtures containing components in the molecular mass range of 150 to approximately 1000. A characteristic fingerprint chromatogram can be generated for a complex mixture of a certain chemistry. By chromatographing standards of compounds whose chemistries are known to be present in the complex mixtures, qualitative structural and compositional information about a given lubricant additive can be determined. These structural and compositional differences are correlated with properties of the additives such as oil solubility, crystallinity and volatility. The value of this analytical methodology lies in its application to product development and quality control.

Compared with HPLC, this SEC method is an attractive technique for analysis of low-molecular-mass mixtures, because of the simplicity of the chromatogram, the reproducibility of the analysis and the qualitative structural as well as compositional information it affords. The simplicity of the SEC chromatograms makes them easier to interpret qualitatively than a corresponding HPLC chromatogram. The utility of this method for characterizing other classes of lubricant additives is possible, but may require calibration with the appropriate relevant standards. Use of this method as a general analytical tool for studying alkylation or oligomerization

chemistry is also possible as long as new standards are established.

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