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Application Note

Rapid Analysis of Antioxidants in Synthetic Lubricants

Jinchuan Yang, Alice J. Di Gioia

Waters Corporation

Abstract

This application note describes a rapid analysis of phenolic and diphenylamine antioxidants in synthetic lubricants using the ACQUITY UPLC System with the PDA Detector.

Introduction

Lubricants are widely used in industrial, automotive, aviation, and marine applications and are critical in the performance of engines, turbines, gears, or other machines. Traditional lubricants are mineral oil-based. Today, synthetic lubricants are gaining more attention because of their superior properties under extreme operating conditions.[1] Antioxidants are major components in the lubricant additive package and have the strongest influence on the useful life of the lubricant.

Analytical techniques that have been applied to analyze antioxidants in lubricants include Liquid Chromatography (LC), Gas Chromatography (GC), Thin-Layer Chromatography (TLC), and Fourier Transform Infrared spectroscopy (FTIR).[2] Using these techniques, analysts can obtain the type and concentration information of antioxidants, which is important in quality control and lubricant monitoring applications. Currently available LC analytical methods are based on large particle size columns (≥5 µm) and were developed more than a decade ago.[3,4] These methods have long analysis times of more than 20 min, and may not provide accurate antioxidant quantification.[5]

Thus, it is desirable to improve this analysis for faster runtime and more accurate quantification. With new solvent delivery design, sub-2-µm column particles, and innovative detector designs, Waters UPLC Technology offers better separation efficiency than HPLC and more sensitive detection. It is an ideal solution for this application.

This application note describes a rapid analysis of phenolic and diphenylamine antioxidants in synthetic lubricants using the Waters ACQUITY UPLC System with the PDA Detector. This methodology provides accurate and reproducible quantification of antioxidant packages with a 6 min total runtime per sample. This reliable and rapid method can assist the antioxidant package QC, and has the potential to be used as a complementary method for determining the remaining useful life of lubricants. In addition, the use of environmentally-friendly solvents,[6] methanol and 2-propanol, combined with fast runtimes and low flow rate, provide additional safety benefits and cost savings in hazardous waste solvent disposal.

Experimental

De-ionized water (Millipore Milli-Q system) and methanol (Fisher Scientific Optima grade) were used as mobile phase A and B. Glacial acetic acid (99.99%) from Sigma-Aldrich was added in both mobile phases at 0.10 vol % as the mobile phase modifier. 2-propanol (Fisher Scientific Optima grade) was used as the sample dissolution solvent. Antioxidants and lubricant commercial product samples were obtained from an industrial collaborator. They were used as received. Figure 1 shows the chemical structures, common names, and CAS Registry numbers of the antioxidants.

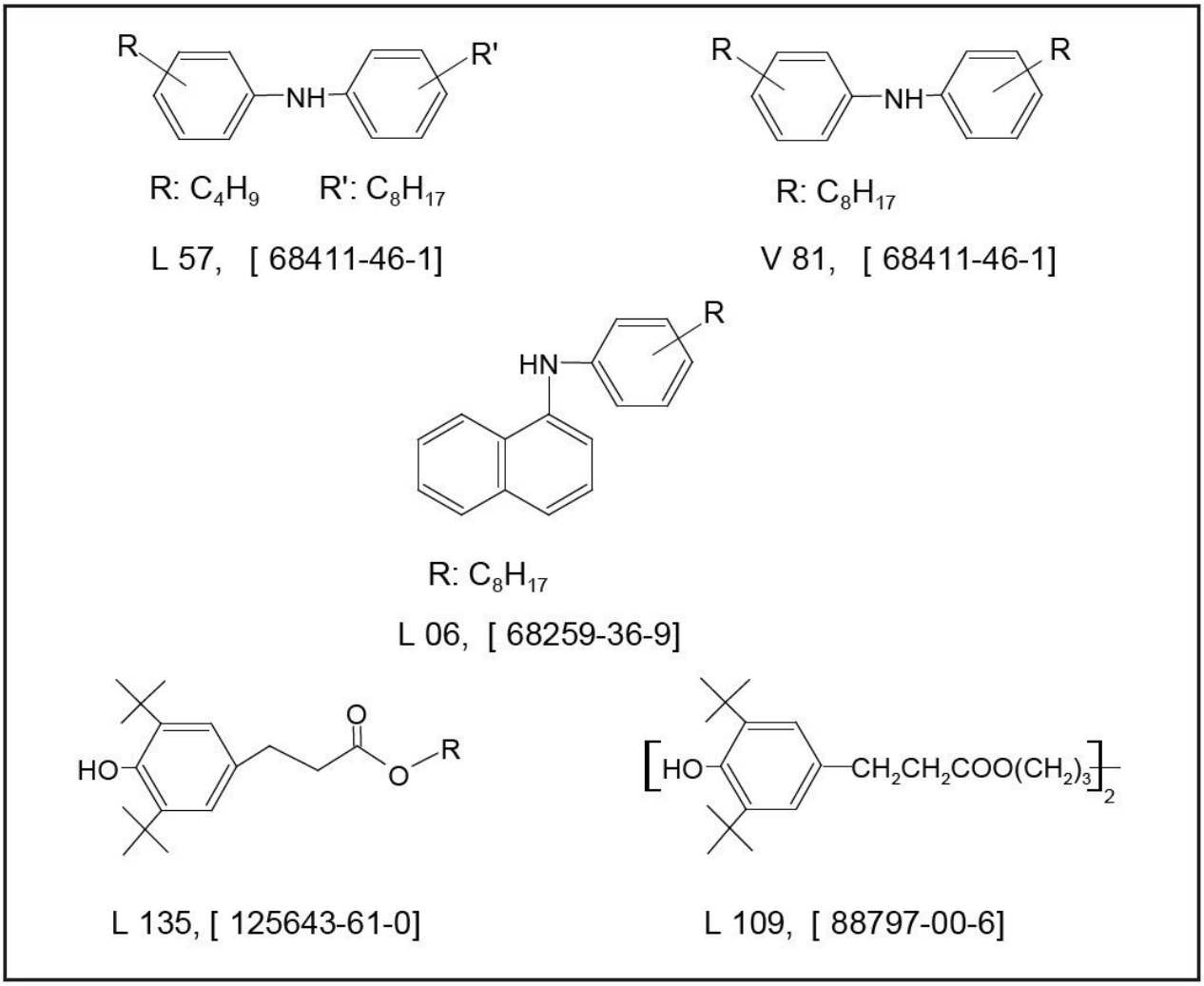

Figure 1. Chemical structures and CAS Registry numbers of antioxidants.

Standard solutions were prepared by dissolving antioxidants in 2-propanol at 1.00 mg/mL as the stock

solution, then standard solutions of 5.00 µg/mL, 20.00 µg/mL, 50.00 µg/mL, 100.00 µg/mL, and 150.00 µg/mL were prepared by serial dilution.

Lubricant samples were dissolved in 2-propanol at 2.50 mg/mL. All samples were filtered through 0.45 µm Acrodisc PTFE Syringe Filter prior to analyses.

UPLC Conditions

LC System:	ACQUITY UPLC with PDA Detector
Software:	Empower 2
Column:	ACQUITY BEH C_8 Column 2.1 x 50 mm, 1.7 µm with online filter
Column temp.:	55 °C
Flow rate:	0.600 mL/min
Mobile phase A:	Water (0.1 vol% acetic acid)
Mobile phase B:	Methanol (0.1 vol% acetic acid)
Needle solvent:	Weak wash solvent: methanol
Strong wash solvent:	2-propanol
Runtime:	4.0 min runtime with 2.0 min next injection delay
Injection vol:	2 µL
Injection mode:	Full-loop injection

Gradient:

Time (min)	%A	%B	Curve
Initial	30	70	6
0.2	30	70	6
1.5	0	100	6
4.1	30	70	11

PDA parameters

Wavelength:	210 nm to 400 nm
Resolution:	1.2 nm
Sampling rate:	10 points/sec
Filter constant:	Normal
Exposure time:	Auto

Results and Discussion

UV Spectrum and Chromatogram

Individual antioxidants were analyzed, and their UV spectra and chromatograms are shown in Figures 2 and 3. Chromatograms were extracted from the PDA data at UV wavelengths of 350 nm (L06), 300 nm (L57 and V81), and 276 nm (L135 and L109) for detection and quantification. The peaks that were used for quantification are also shown in Figure 3.

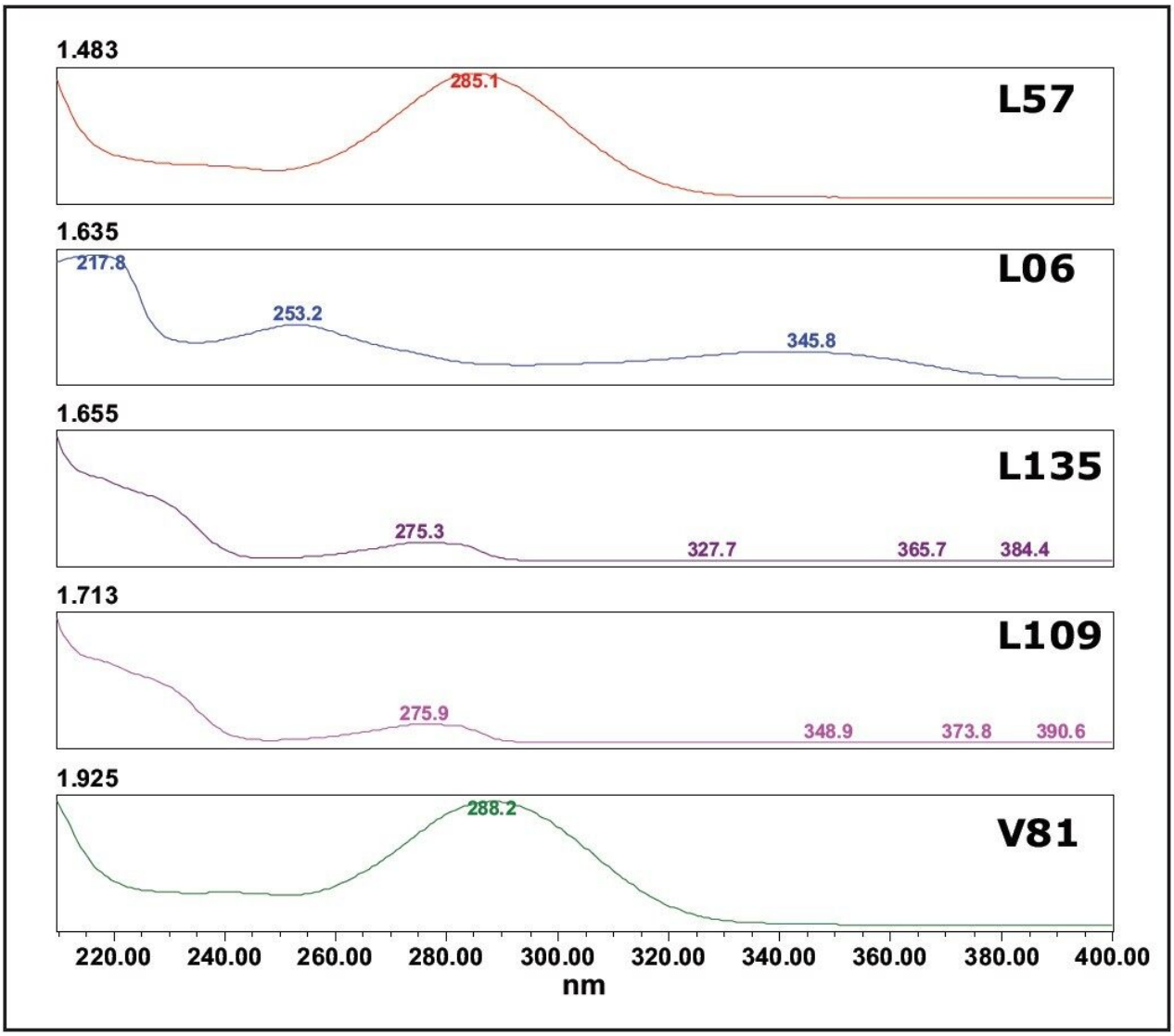

Figure 2. UV spectra of antioxidants obtained with the ACQUITY PDA in reversed-phase UPLC. Standard solutions are at concentration of 1.0 mg/mL.

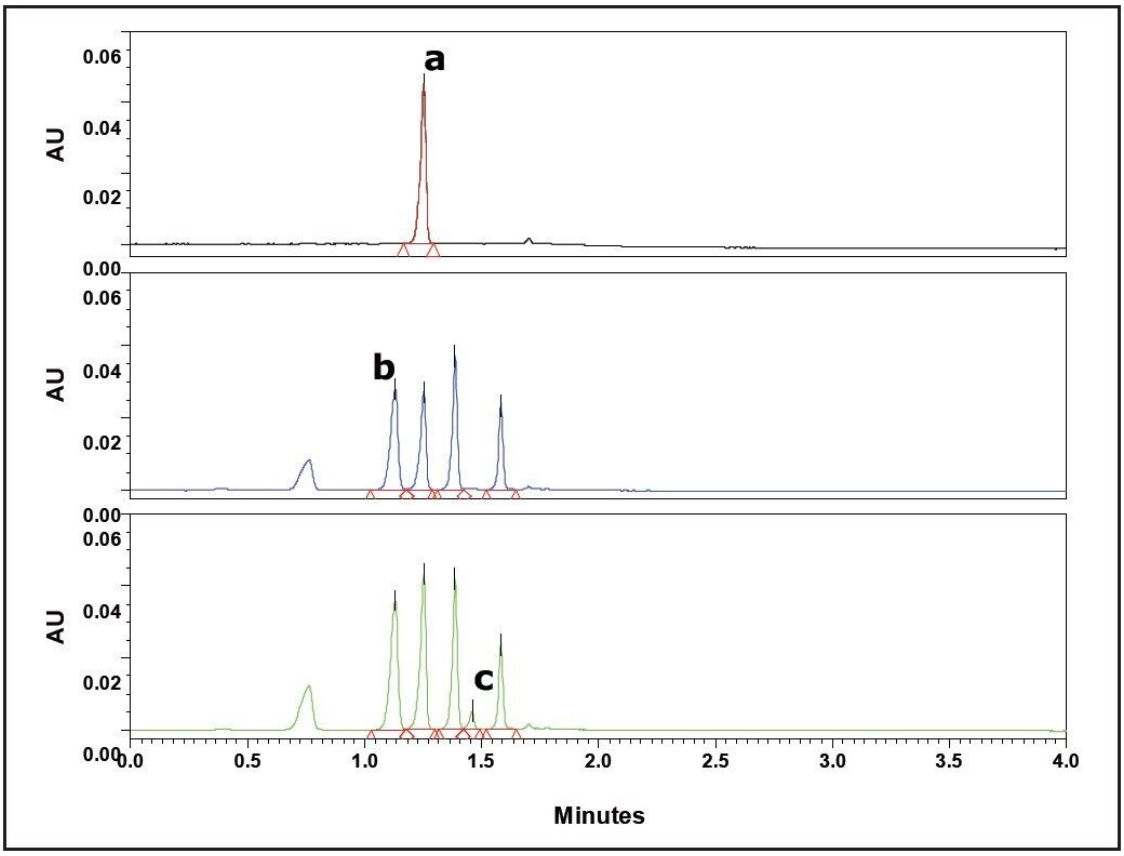

*Figure 3. Chromatograms of antioxidants extracted from PDA 2D data at their characteristic UV wavelength. The antioxidant, wavelength, and peak used for quantification (marked by *) are shown in the chromatograms.*

A runtime of 4 min was necessary to allow the base lubricant to elute from the column. An Evaporative Light Scattering Detector (ELSD) was used in tandem with the PDA Detector to monitor the elution of the base lubricants. Peaks were observed eluting from the column until 3.5 min (data not shown). Therefore, a 4.0 min run was necessary to ensure reproducible chromatography. During approximately 400 injections, only 1.4% column pressure fluctuation was observed, which indicated no adsorption on column.

Quantification

Antioxidants L109, L06, and L57 were quantified by using characteristic peaks in the specific UV chromatograms. However, the quantification of antioxidants L135 and V81 may be complicated by the existence of L57, since L57's two main peaks at retention times of 1.38 min and 1.57 min overlapped with L135 and V81 peaks. When the concentration of V81 and L135 are to be determined, the potential interference from L57 must be considered. This potential interference can be eliminated by using the Custom Field

Calculations feature in Empower 2 Software.[7]

Calibration data of the peak area versus concentration for antioxidants were fit by least squares linear regression at concentrations from 5 µg/mL to 150 µg/mL, as shown in Figure 4. The square of the correlation coefficients (R^2) and calibration equations are also shown in Figure 4. Excellent linearity was obtained (R^2 > 0.9997).

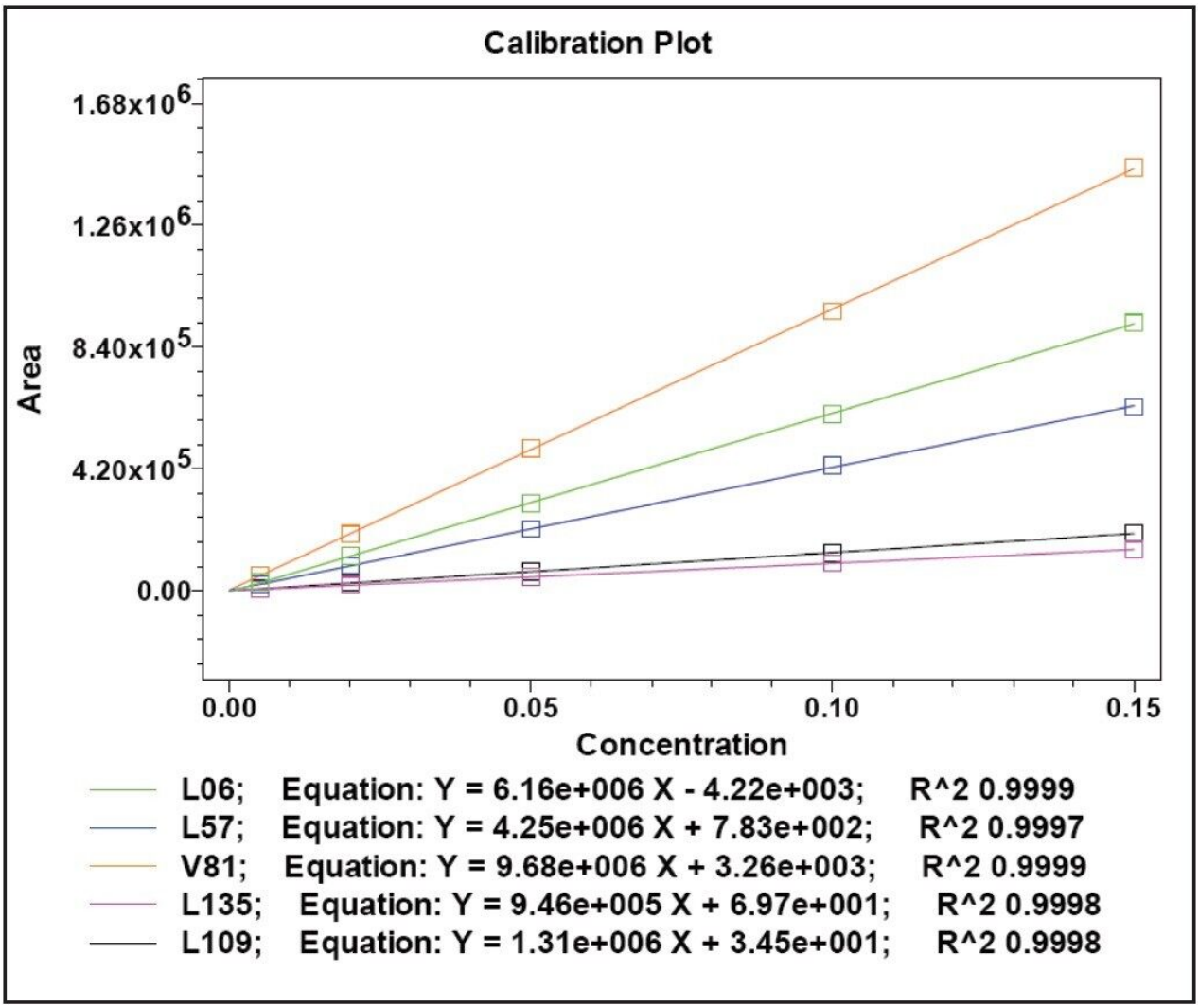

Figure 4. Calibration plots of peak area versus sample concentration for antioxidants. The linear equation and square of correlation coefficients are listed under the plot.

Sensitivity was estimated by using the signal-to-noise (S/N) ratio at the lowest concentration (5 µg/mL). The Limit of Quantification (LOQ at S/N=10) for these antioxidants varied as much as 20 times. The highest LOQ (the least sensitive) was estimated at 1 µg/mL (with 2 µL injection volume).

Reproducibility and Accuracy

The quantification results for the four lubricant samples are shown in Table 1. The chromatograms for Lubricant C are shown in Figure 5.

	RT (min)	RT %RSD n=6	Wt. %	Rel. Std. Dev. (Intra-day, n=6)	Rel. Std. Dev. (Inter-day, n=4)
Blend C					
L06	**1.252**	**0.17**	**0.52**	**<0.46%**	**0.47%**
L109	**1.457**	**0.12**	**0.23**	**<2.96%**	**3.60%**
L57	**1.129**	**0.21**	**0.59**	**<0.27%**	**0.30%**
Blend D					
L135	**1.375**	**1.06**	**0.62**	**<3.93%**	**2.52%**
L57	**1.129**	**0.24**	**1.05**	**<0.59%**	**0.18%**
Blend E					
L06	**1.252**	**0.27**	**0.35**	**<0.62%**	**0.79%**
V81	**1.581**	**0.21**	**0.74**	**<0.53%**	**0.16%**
Blend F					
L57	**1.129**	**0.23**	**5.91**	**<0.47%**	**0.15%**

Table 1. Quantification results for lubricants.

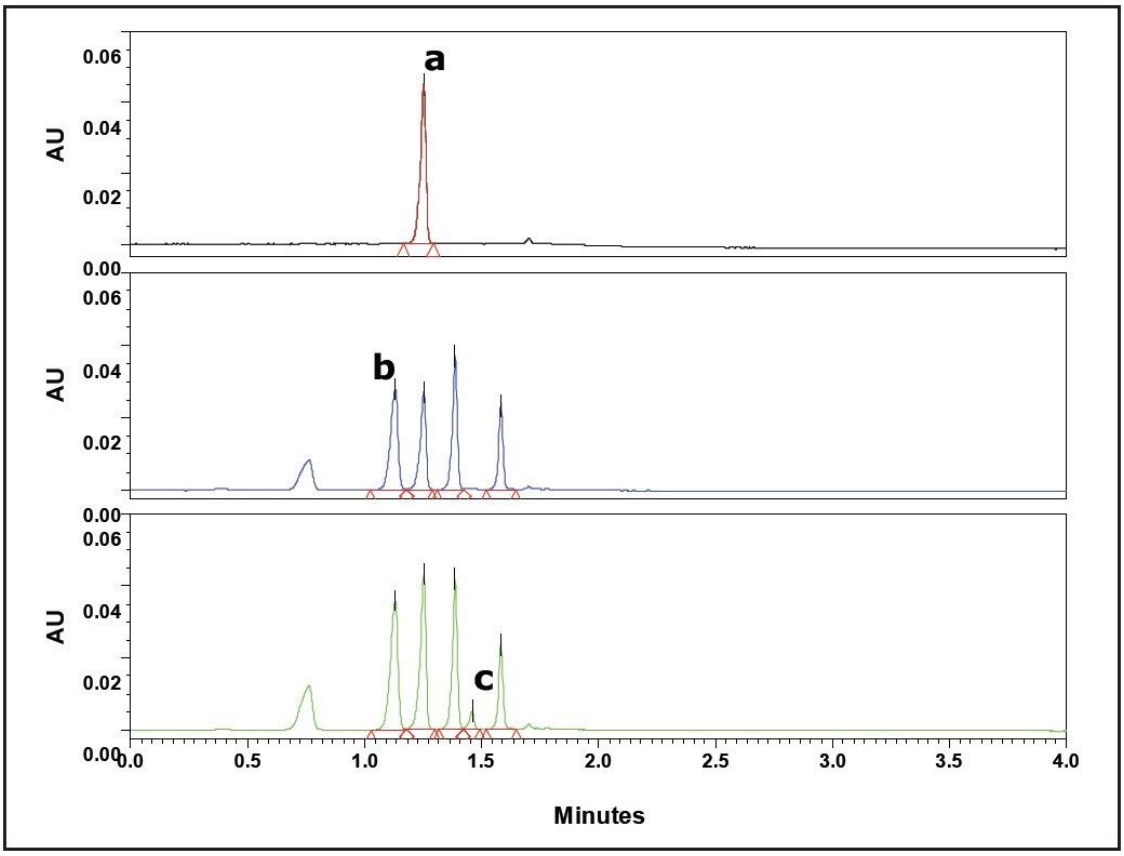

Figure 5. Extracted chromatograms for Lubricant C at 350 nm, 300 nm, and 276 nm. Peaks a, b, and c are the quantification peaks for L06, L57, and L109, respectively.

Repeated analyses of these samples showed good reproducibility. A typical relative standard deviation of less than 1% was obtained for both intra- and inter-day measurements, except the L109 in Sample C and the L135 in Sample D, which had relative standard deviations of less than 4%. The relative standard deviations in retention time are also shown in Table 1.

The accuracy of this method was tested by spiking sample C with antioxidants (L06, L109, and L57) and measuring the changes in antioxidant concentration before and after spiking. By comparing the concentration change and actual amount of antioxidant that was added into the sample, we can evaluate the accuracy of this method. The results show less than 5% relative errors (Table 2), which is better than the 10% error found in the literature.[3]

Antioxidant	Spiked amount (wt%)	Measured (wt%)	Rel. Diff. (%)
L06	0.43	0.416	-3.3
L109	0.46	0.450	-2.1
L57	0.43	0.412	-4.1

Table 2. Determination of spiked antioxidant levels in a lubricant.

Conclusion

Waters ACQUITY UPLC System with PDA detection provides an ideal solution for lubricant antioxidant analysis. Rapid, accurate, and reproducible quantification of antioxidants in synthetic lubricants has been demonstrated. This analytical method is about three times faster, and consumes six times less solvent than current methods. In addition, the use of environmentally-friendly solvents brings additional safety benefits to users.

By adopting this method, analysts can obtain more precise control of the antioxidant levels in lubricants, which in turn will result in extended service intervals, and thus reduce the lubricating system's maintenance costs. This method has broad applications for lubricant analysis labs, lubricant additive manufacturers, and industries where lubrication is a major factor in the daily operations.

References

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2. E R Booser. CRC Handbook of Lubrication and Tribology, Volume III: Monitoring, materials, synthetic lubricants, and applications. CRC Press LLC, Boca Raton, FL, 1994.
3. M A Keller and C S Saba. *J. Chromatogr.* 409: 325–335, 1987.
4. S V Greene and V J Gatto. Proceedings of International GPC Symposium '98. Waters, Milford, MA, pp. 612, 1999.
5. Private communication with users.

6. K Alfonsi, J Colverg, *et al. Green Chemistry* 10: 31–36, 2008.

7. Two custom fields were created for the quantification of L135 and V81.

Area_L135 = Area-CConst1 × CCompRef1[Area]

Area_V81 = Area-CConst2 × CCompRef1[Area]

Where Area_L135 and Area_V81 are the corrected peak areas (without L57's interference) for L135 and V81, respectively; Area is the peak area; CConst1 and CConst2 are the peak area ratios of the L57's peak at 1.38 min and 1.57 min over the reference peak (L57's peak at 1.13 min) in UV 276 nm and UV300 nm channels, respectively. The CCompRef1[Area] is the peak area of the reference peak (L57's peak at 1.13 min).

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