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アプリケーションノート

LC/APCI-MS Analysis of Antioxidants from Lubricating Oil

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Abstract

This application note demonstrates LC/APCI-MS analysis of antioxidants from lubricating oil.

Introduction

Among various kinds of additives in lubricating oil, antioxidants are the most important ones. They can extend the lifetime of the lubricating oil by reducing the oxidation reactions. Nowadays, instead of applying single antioxidant, a package containing a mixture of antioxidants is usually used to obtain optimum effect. LC/API-MS has become an important tool for analyzing these mixtures in petrochemical research. All work shown in this application note was done on Waters Alliance ZMD LC-MS System. Results were obtained with FIA-MS and LC-MS methods, which are simple, fast and highly efficient, using on-the-fly positive-negative switching and in-source CID (collision-induced dissociation).

Experimental

Experimental Conditions

LC-MS:	Waters Alliance System: 2690 Separations Module, 996 Photodiode Array Detector, ZMD 4000 Mass Detector
Column:	Symmetry C_{18} , 2.1 x 150 mm, 5 mm, 1 mL/min at 30°C
Mobile phase:	Acetonitrile/water (99:1)
PDA detection:	20–450 nm, 1.2 nm resolution
MS detection:	APCI+/APCI-, full can *m/z* 100–750
Desolvation:	550 °C
Cone Voltages:	30, 40, 50, 80V

Results and Discussion

APCI-MS Parameter Optimization by Flow Injection Analysis

APCI-MS optimization was done on the sample with positive and negative switching within a single run via flow injection analysis. A series of ions with *m/z* of +170, 226, 282, 338, 394 indicated the existence of -C_4H_9 (loss of *m/z* 56). Two other peaks with *m/z* value of 659 and 642 indicated that this sample consists at least 3 different types of compounds.

APCI+: Figure 1 shows the total ion chromatogram of APCI+ scan with peaks A,B,C,C’ ,D,E. It was determined that these compounds belong to aromatic amine series with the help of IR (infrared) and elemental analysis. The main frame of the structure should be R-Ph-NH-Ph-R’ . The molecular weights were easily determined from the MS data.

Structural study by LC/APCI-MS

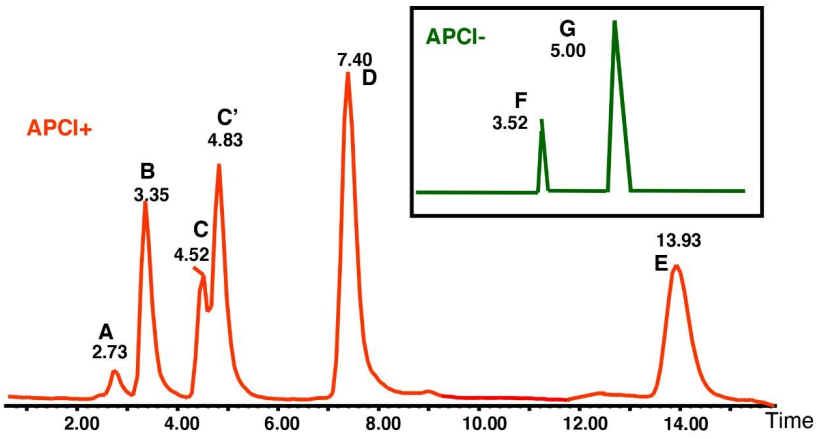

Figure 1. Chromatograms.

APCI-: In Figure 1, Peaks F and G were from an APCI- scan. Peak F is zinc dialkyl disulfide phosphate (ZDDP) with MW 658. This was confirmed by in-source CID as shown in Figure 2. Peak G (MW 642) was sulfureted-phenolic antioxidant.

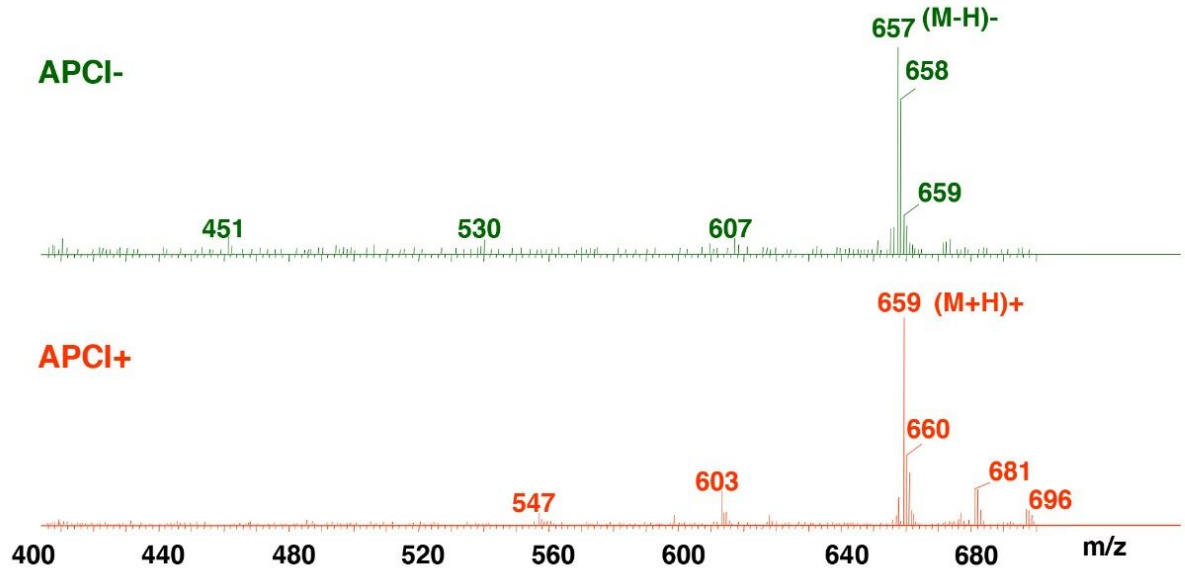

Figure 2. Positive/Negative Mass Spectral Scans of Peak F.

All the detailed information about the compounds in the mixture are listed in Table 1.

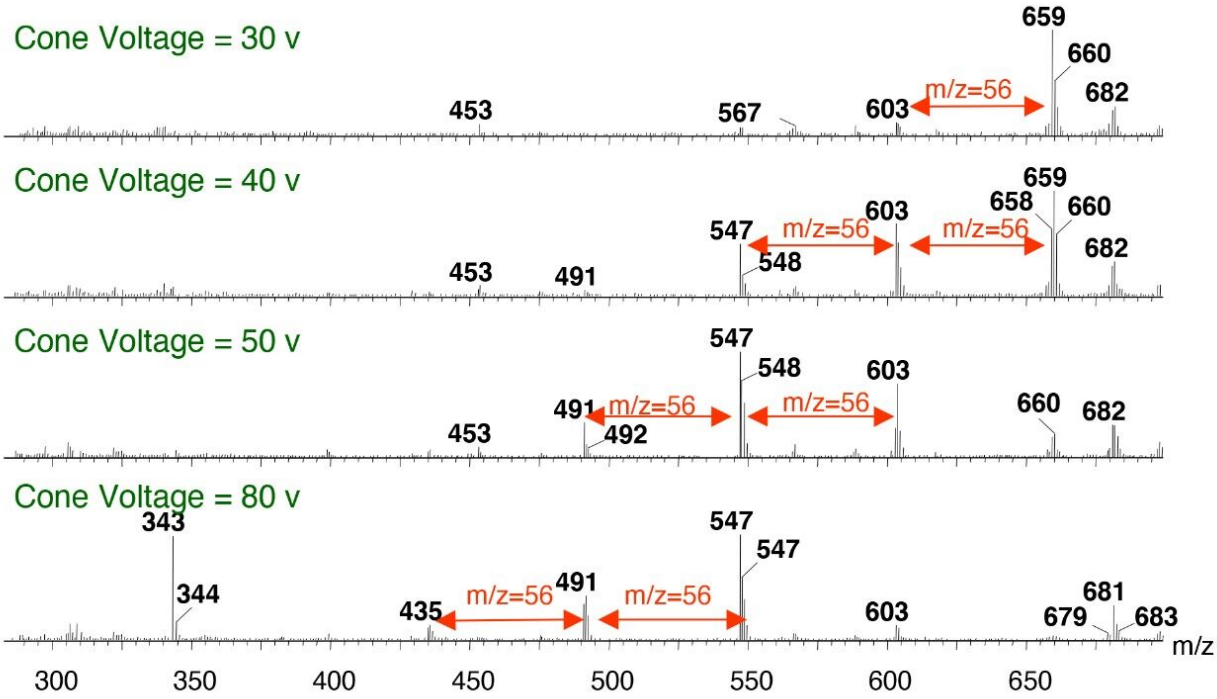

Figure 3. Mass Spectra of Insource CID with Different Cone Voltages for Peak F.

The Waters Alliance LC-MS system has the capability of on-the-fly positive/negative switching during a run. Spectra from APCI- and APCI+ can be obtained from a single injection. This saves time during methods development and sample analysis. The spectra for Peak F are shown here.

In-source collision-induced dissociation (CID) cause molecules to fragment. Increasing the cone voltage increases the number fragments. The loss of *m/z* 56 is the loss of C_4H_9. This loss is indicated by the arrows. The fragmentation patterns can be used to confirm the structures of ZDDP, zinc dialkyl disulfide phosphate.

Peak ID	RT(min)	m/z +	m/z -	MW
A	2.73	170.2	-	169
B	3.35	226.3	-	225
C	4.52	282.2	-	281
C’	4.83	282.2	-	281
D	7.40	338.4	-	337
E	13.93	394.3	-	393
F	3.52	659.1	657.1	658
G	5.00	-	641.7	643

Table 1. Characterization of Each Compound from the Mixture.

The structure for each peak is shown for peaks A, B, C, C’ , D, E, G. Peak F is zinc dialkyl disulfide phosphate.

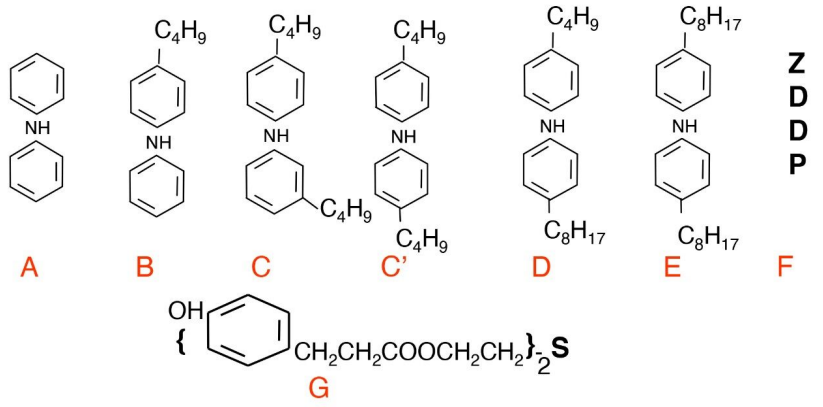

Figure 4. The Structures of the Compounds.

Conclusion

The Waters Alliance ZMD LC-MS System is suitable for analysis of complex samples. With on-the-fly positive/negative switching and in-source CID, multiple data sets can be obtained from a single injection. This permits faster information collection with better sensitivity.

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