Applikationsbericht

Rapid, Direct Analysis of Additives in Mineral Oils with RADIAN ASAP

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This is an Application Brief and does not contain a detailed Experimental section.

Abstract

In this application note, the suitability of a fast and direct analytical method was assessed for qualitative analysis of chemical additives in mineral oils using the Waters RADIAN™ Atmospheric Pressure Solids Analysis Probe (ASAP) mass detector.

Benefits

Direct analysis of additives in lubrication oils for quality control of final products following simple system operation and data interpretation, minimal sample preparation (sample dilution), with no requirements for chromatographic separation of compound of interest.

Introduction

Mineral oils are petrochemical products resulting from crude oil distillation and are mostly used to lubricate engines or machinery parts to decrease friction, maximize efficiency, and protect mechanical components. In addition to these, mineral oils designed for automotive uses also help protect against corrosion, prevent sludge accumulation, eliminate, or reduce contaminants, and cool the engines.

Mineral oils naturally degrade over time due to oxidation and decomposition. To prevent this and to enhance the oil performance, various chemical additives are added to the base oil. Common additives used are antioxidants, corrosion inhibitors, detergent/dispersant, anti-wear, anti-foam, alkalinity, and viscosity improvers.[1] Usually most motor oil contains between 15–30% oil additives. The analysis and continuous monitoring of lubricant oil formulations is a critical step in lubricant oil manufacturing and in understanding the chemical composition and degradation in performance of lubricant oils as they age over time. As an example, it is important for formulation laboratories to have a clear understanding of the oil composition. This is a challenging task as mineral oils have complex chemical profiles and selecting appropriate analytical technology suitable for this is critical to ensure confident results with appropriate timescales. Given the complexity and variety of chemicals present in a mineral oil sample, traditionally analytical technologies such as liquid chromatography (LC) or gas chromatography (GC) coupled to nominal mass or high-resolution mass spectrometer (MS) detectors are used. However, although advantageous, such techniques are time consuming and require a certain degree of sample preparation which can add to the cost of analysis and affect the sample throughput in quality control laboratories. In this application note, a rapid and direct analytical method was develop and tested for confident determination of various mineral oil additives using RADIAN ASAP mass detector, a single quadrupole mass spectrometer combined with the Atmospheric Pressure Solids Analysis Probe (ASAP) in a compact footprint.

Experimental

Two commercially available mineral oil samples (S444137 and S444192) were analyzed following a simple dilution step to a final concentration of 0.1 mg/mL using 9:1 toluene:methanol with 0.1% formic acid.

Diluted samples were then analyzed using the sealed glass capillary (Figure 1). Separate glass capillaries were used for each sample. Each glass capillary was analyzed as capillary blank first and as solvent capillary blank (capillary dipped in the solvent used to dilute the mineral oil samples) prior to loading the diluted liquid oil samples.

Figure 1. The Waters RADIAN ASAP Direct Mass Detector.

Analytical configuration: The analytical instrumentation used was a Waters RADIAN ASAP operated in positive and negative ASAP mode, more details of the parameters used in the analytical method are given in Table 1. Samples were introduced into the corona discharge region of the RADIAN ASAP on a sealed glass rod and volatilized by stream of heated nitrogen. Gaseous analyte molecules were ionized by nitrogen plasma prior to being guided into the instrument and analyzed by the single quadrupole analyzer equipped with a photomultiplier detector. Instrument control as well as data acquisition and processing were performed with MassLynx™ 4.2 Software.

Instrument parameter	ASAP+	ASAP-
Corona current (μA)	3	2.5
Cone voltage (V)	15	15
Scan speed (Hz)	1.0	1.0
Mass range (*m/z*)	50–1200	

Table 1. RADIAN ASAP acquisition method

Temperature gradient

Step temperature (°C)	Hold time (min)	Total time (min)
100	0.5	0.5
200	0.5	1.0
300	0.5	1.5
400	0.5	2.0
500	0.5	2.5
600	2.5	5.0

Results and Discussion

The mineral oil samples were introduced into the RADIAN ASAP source using a disposable glass capillary from the front of the instrument. The nitrogen plasma indirectly creates ions from the volatilized molecules which are then guided into the instrument and sorted based on differing mass to charge (*m/z*) ratio before being detected and generating the mass spectrum. A typical total ion chromatogram (TIC) profile of a mineral oil sample analyzed using a ramped temperature program is shown in Figure 2.

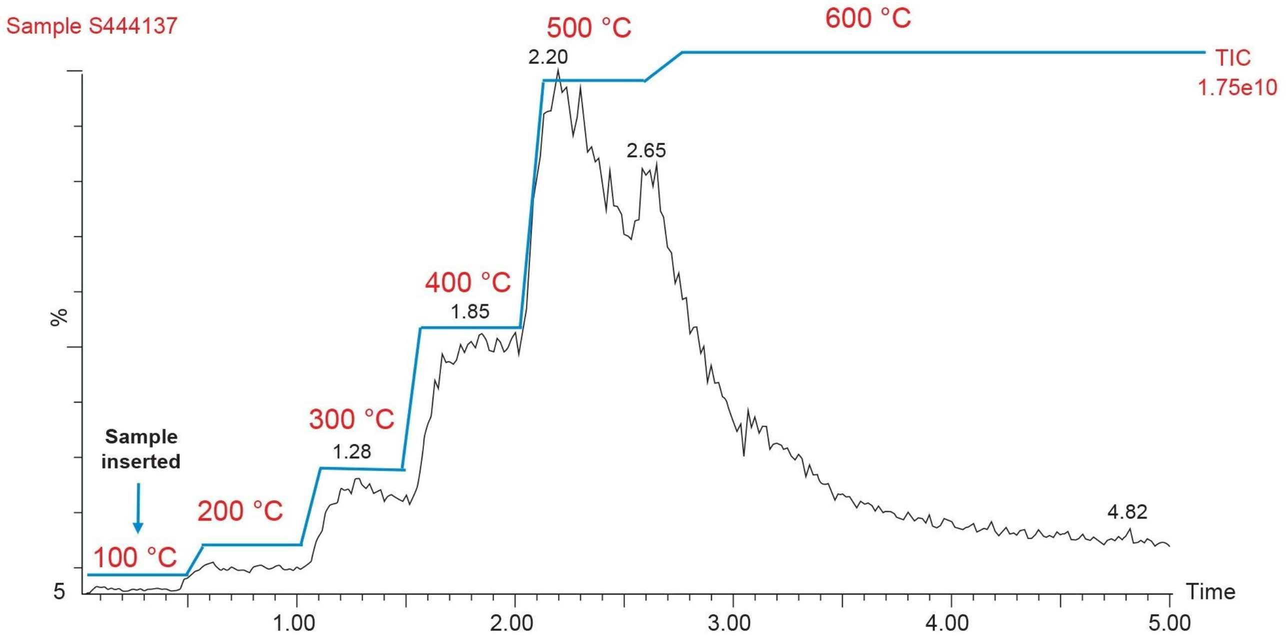

Figure 2. TIC (ASAP$^+$ ionization mode) examples of a mineral oil sample (S444137) analyzed using the RADIAN ASAP Direct Mass Detector.

Sample carryover is a major problem that can affect the analytical measurement, especially for complex samples such as mineral oils. Negligible sample to sample carryover was observed after analyzing a mineral oil sample. An example of the total ion current (TIC) chromatogram for a carryover assessment is shown in Figure 3.

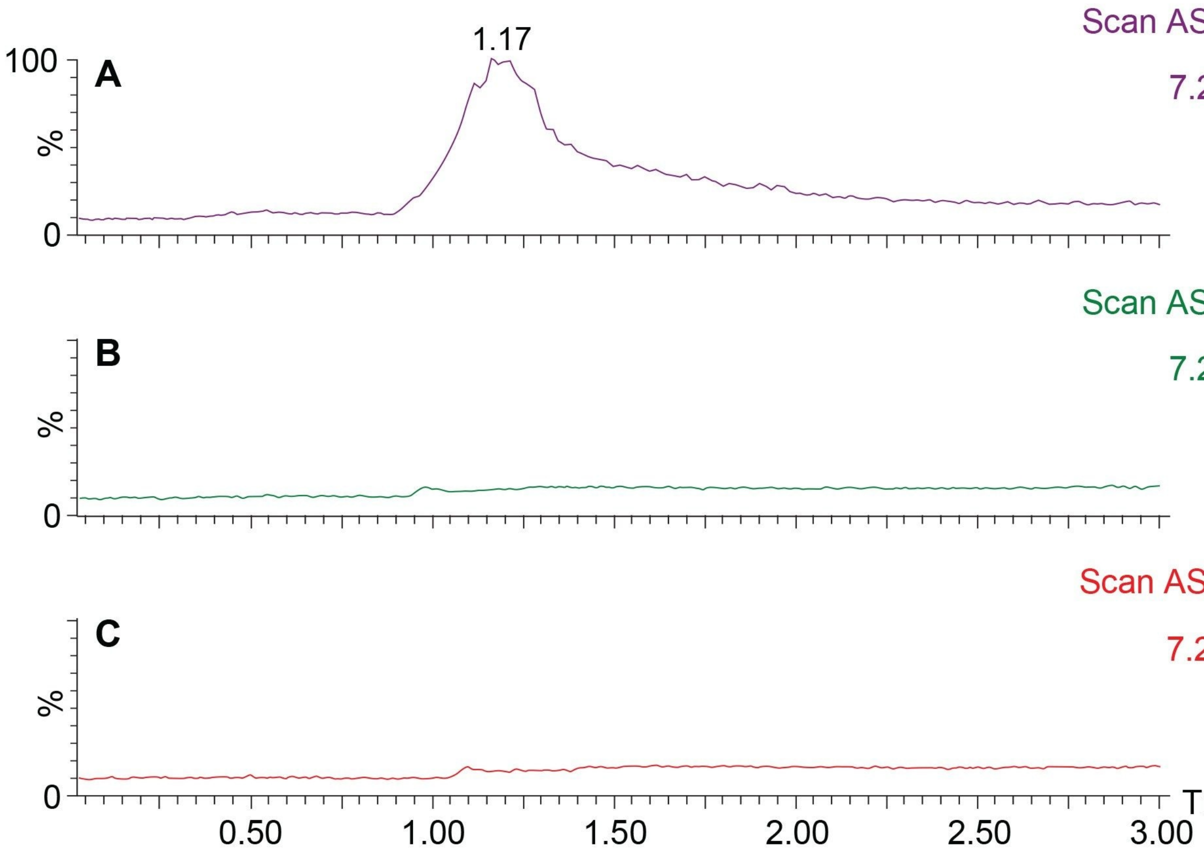

Figure 3. Carryover assessment following the analysis of mineral oil sample S444192 (A) analyzed in ASAP$^+$ ionization mode. No compounds carry over was observed when using the same capillary dipped in solvent (B) or as capillary blank (C).

Antioxidants and base oil were successfully detected in positive ASAP ion mode in both mineral oil samples S444137 and S444192 (Figure 4). Sample S444137 contained mostly tert-butylhydroquinone (as *m/z* 167 $[M+H]^+$) and a phenolic antioxidant (*m/z* 390) as compared to sample S444192 which had additionally an amine containing antioxidant, identified as di-nonyl diphenylamine (*m/z* 422 $[M+H]^+$). These have been previously reported with protonation of amine-based antioxidants common when traces of polar solvents (such as methanol or water) are present and act as proton donors.[2,3]

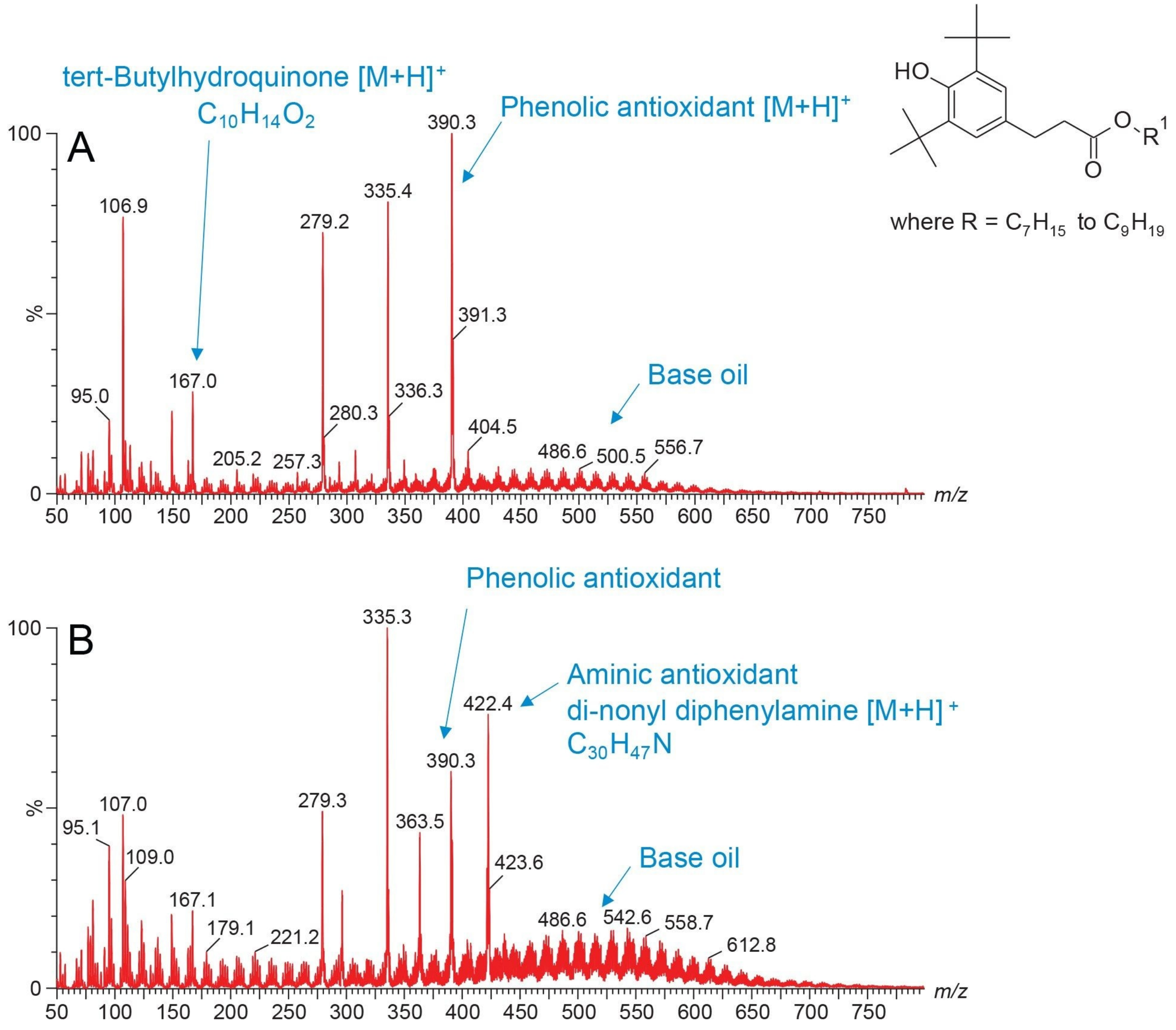

Figure 4. Positive ASAP$^+$ spectra showing the main chemical components of two mineral oil samples: S444137 (A) and S444192 (B).

In addition to positive ASAP ionization mode, the mineral oil samples were also acquired in negative ASAP ion mode (ASAP$^-$). Mostly [M-H]$^-$ deprotonated species were observed with dominant additive ions corresponding to phenolic antioxidant ions *m/z* 389, Zn dithiophosphate (*m/z* 241 and *m/z* 255), alkyl salicylate (*m/z* 333 and *m/z* 361), and sulfur coupled phenols (*m/z* 533). The ASAP$^-$ data indicated that sample S444137 contained mainly Zn dialkyldithiophosphate, phenolic antioxidant, and sulfur coupled phenol whereas sample S444192 had high amounts of Zn dithiophosphate, phenolic antioxidant, and alkyl salicilate (Figure 5).

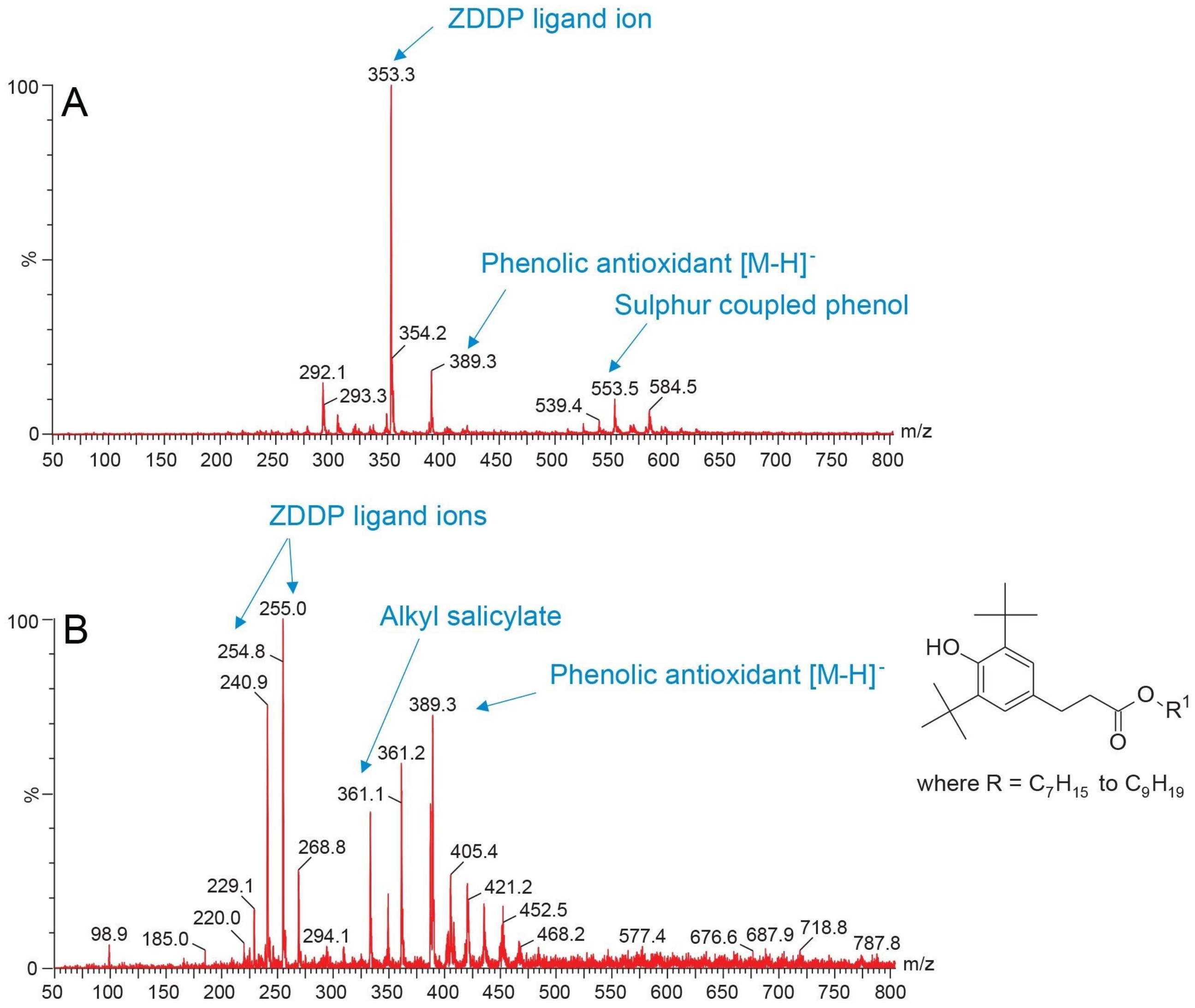

Figure 5. Negative ASAP⁻ spectra of showing the main chemical components of two mineral oil samples: S444137 (A) and S444192 (B).

Conclusion

A rapid, direct method has been employed to analyze the additive content of commercially available mineral oil samples using the Waters RADIAN ASAP mass detector. The results indicate that this method provides a broad coverage of a variety of chemical components of interest in commercial mineral oil samples. Phenolic, zinc and aminic antioxidants, sulfur-based phenols, as well as the base oil components were detected in the mineral samples.

The RADIAN ASAP enables rapid, low cost-per-sample analysis of mineral oils and provide analytical results with a minimum of training or mass spectrometry knowledge, making it suitable for fast pace quality control or formulators laboratories. These laboratories can easily detect key chemical components in mineral oil samples and speed up the decision-making process. Features including thermal gradient analysis are suitable for such complex samples and enable fast generation of analytical results using an uncomplicated method.

References

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3. Riches E, Da Costa C. RADIAN ASAP for Quick and Simple QC Screening for Additives in Lubricant Oils. Waters Corporation Application Note 720007090, 2020.

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RADIAN ASAP Direct Mass Detector <https://www.waters.com/waters/nav.htm?cid=135073413>

MassLynx MS Software <https://www.waters.com/513662>

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