Analysis of Polymer Antioxidant Additives on the Agilent 500 Ion Trap LC/MS

Application Note

Materials Testing and Research

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Abstract

This note demonstrates the quantitative analysis of three commonly used antioxidant polymer additives, namely butylated hydroxyl anisole (BHA), Ethanox 330, and Irganox 1010 using the Agilent 500 Ion Trap LC/MS. This instrument provides excellent MS/MS and full scan sensitivity.

Introduction

Plastics are widely used and they vary in their application, ranging from automobile parts, components for houses and buildings, and packaging for everything from food to electronic parts. The diverse applications of plastics are credited to the incorporation of additives. These additives improve the performance characteristics of the polymer resins.

As the structure of polymers has become more and more complex, there has been an increasing need for reliable analysis of additives to meet more exacting performance demands. Accurate and precise analytical methods are required for the manufacture of high quality products. The analytical needs for additives analysis are qualitative identification, screening for potential contaminants (non-target analysis), and reliable, accurate quantitative determination of additive concentration in a complex matrix (typically down to 0. 1 wt% or less in the plastic material). A considerable analytical challenge is the ability to provide all of this information in a single analytical run.

An ion trap mass spectrometer is well suited for this analytical challenge, as it provides excellent full scan and high mass sensitivity along with true MS/MS capability. Both target additives and non-target contaminants can be reliably detected and quantitated in a complex matrix. This application note uses the Agilent 500 Ion Trap LC/MS to demonstrate the quantitative analysis of three commonly used antioxidant polymer additives, namely butylated hydroxyl anisole (BHA), Ethanox 330, and Irganox 1010. Figure 1 shows the chemical structures for these common additives.

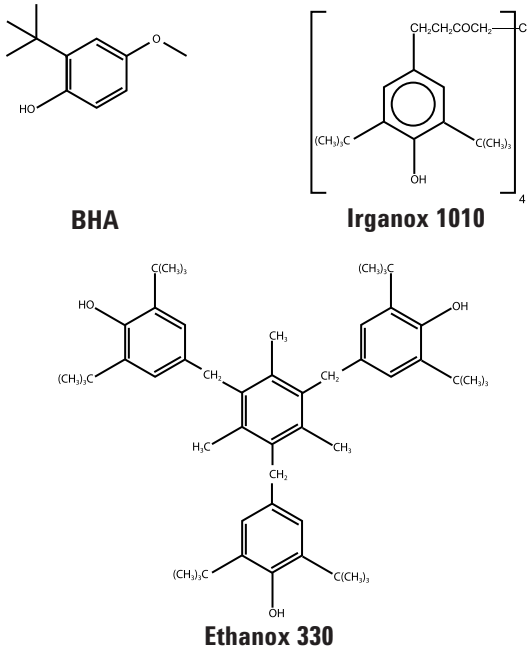

Figure 1. Structure of studied antioxidant additives.

Instrumentation

- Agilent 500 Ion Trap LC/MS, equipped with an APCI source and built-in syringe pump.
- Agilent ProStar 210 Binary Solvent Delivery Modules
- Agilent ProStar 430 AutoSampler

Materials and Reagents

BHA (B1253) was purchased from Sigma-Aldrich, Milwaukee, WI. Ethanox 330 (PLAS-CAL-002-3) was purchased from AccuStandard, New Haven, Connecticut and Irganox 1010 was provided by Ciba Specialty Chemicals, Tarry Town, New York. Methanol, dichloromethane and isopropanol are HPLC grade and provided by Fisher Scientific Co, Fair Lawn, NJ.

Sample Preparation

A stock solution of BHA was prepared in methanol and dilutions for the calibration curve were made in methanol. Ethanox 330 was supplied in isopropanol and the dilutions for the calibration curve were made in isopropanol. The stock solution of Irganox 1010 was made in dichloromethane and it was further diluted in methanol for calibration. The concentration ranges prepared were typically from 5–800 pg/µL.

HPLC Conditions

Column	Agilent Microsorb-MV, C8, 4.6 × 50mm, 3.5 µm Agilent p/n R0086300F3			
Solvent A	Water			
Solvent B	Methanol			
LC program	Time (min:sec)	%A	%B	Flow (mL/min)
	00:00	40	60	1
	10:00	0	100	1
	15:00	0	100	1
	15:01	40	60	1
	20:00	40	60	1
Injection Volume	5 µL			

MS Parameters

Ionization mode	APCI
Ion polarity	Negative
Trap damping gas	0.8 mL/min
Corona current	–10 µA
API drying gas	14 psi at 400 °C
API nebulizing gas	Air at 60 psi
Shield voltage	–600 Volts

MS/MS Parameters

Analyte	Transition (*m/z*)	Amplitude Excitation (volts)	Scan range (*m/z*)
BHA	179.5 → 164.5	1.75	100–175
Ethanox 330	773.8 → 717.0	1.70	256–784
Irganox1010	1176 → 958	2.0	389–1000

Results and Discussion

The additive content of plastics needs to be monitored for quality and regulatory reasons. Some of the regulations with limits are food-contact plastic articles intended for repeated use (21 CFR 177.2600) and food contact packaging for irradiated food (21 CFR 179.45)

When it comes to identifying these antioxidants, it is obviously important to obtain spectra that verify the molecular weight and demonstrate that the starting material is free from degradation. The Agilent 500 Ion Trap LC/MS has excellent full scan sensitivity as demonstrated in Figure 2. Irganox 1010 has an $[M-H]^-$ ion at *m/z* 1175.9 and is very intense in the spectrum generated on the 500 Ion Trap.

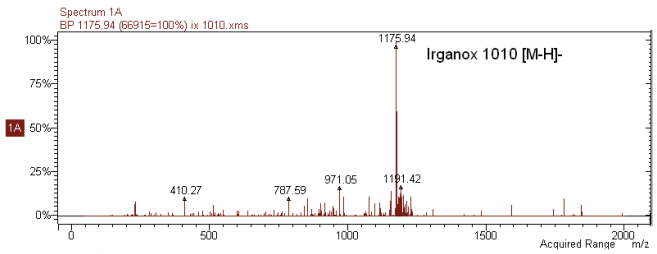

Figure 2. Irganox 1010 infused at 500 pg/µL on the Agilent 500 Ion Trap in full scan mode (50–2000 amu).

Figure 3 is an example of the type of product ion spectrum that can be obtained with the 500 Ion Trap, which is rich in detail and provides the user with structural information and confirmation of its identity in a complex matrix.

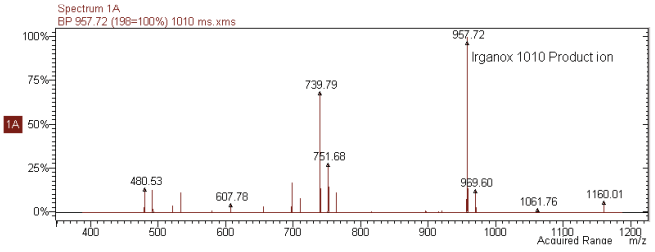

Figure 3. MS/MS product ion spectrum of Irganox 1010 on the 500 Ion Trap. 500 pg/µL infusion.

Although in-source CID can be used for generating fragments on single quadrupole instruments, one must be concerned with the quality of the spectra obtained, since the skimmer-CID is not truly selective against the matrix. The 500 Ion Trap provides true MS/MS, totally eliminating the effect of matrix and therefore adding increased confidence in the analytical results.

The MS/MS chromatograms of the three antioxidant additives studied are given in Figure 4. Many of these compounds have similar structures and co-elute on HPLC columns, thus increasing the need for selective MS/MS detection.

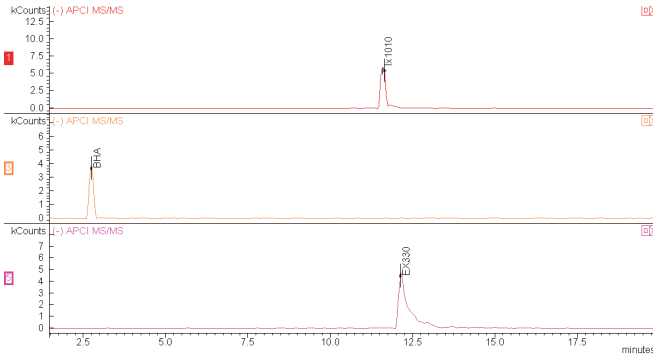

Figure 4. MS/MS chromatograms of Irganox 1010, BHA and Ethanox 330 on Microsorb-MV C8 column (200 pg/µL each component).

Calibration linearity is demonstrated in Figure 5 for BHA in MS/MS mode. The curve has an R^2 value of 0.998 and an RSD of 12.3%. LOQ values for pg quantities on column are shown in Table 1.

The antioxidant additive concentration incorporated in plastics is typically 0.1 % by weight (K. Figge and Freytag, Food Additives and Contaminants V.1, n 4, 1984) - quite high in concentration relative to the very low detection limits reported here (40 pg on column). This excellent sensitivity enables the user to have more flexibility in the sample preparation process by allowing the use of smaller sample size and/or the ability to dilute the sample prior to analysis. In addition, the superior full scan sensitivity of the 500 Ion Trap provides reliable information about potential impurities.

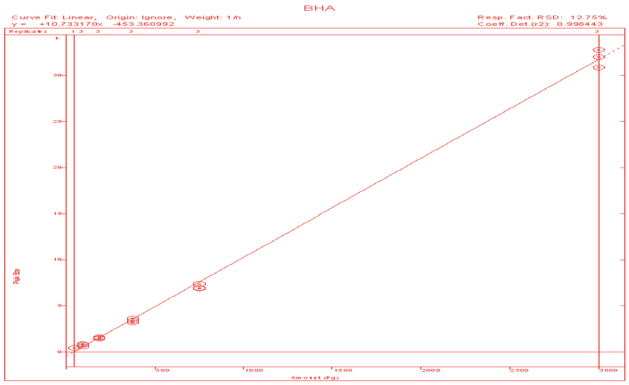

Figure 5. BHA Calibration curve (full scan MS/MS negative APCI) 40–3000 pg on column.

Table 1. LOQ for Antioxidant Additives

Compound	LOQ
BHA	100 pg
Ethanox	330 78 pg
Irganox 1010	250 pg

Conclusion

- The Agilent 500 Ion Trap LC/MS provides excellent full scan sensitivity and MS/MS making it an ideal tool for the screening and quantitative analysis of antioxidant polymer additives.
- Information rich MS/MS spectra eliminate false positives.
- Low limits of quantitation and excellent linearity have been demonstrated.

References

1. K. Figge and W. Freytag, Additive migration from various plastics with different processing or properties into test fat HB 307., Food Additives and Contaminants v.1, n.4, 1984
2. 21 CFR 177.2600
3. 21 CFR 179.45

For More Information

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