Waters Integrity System Applications

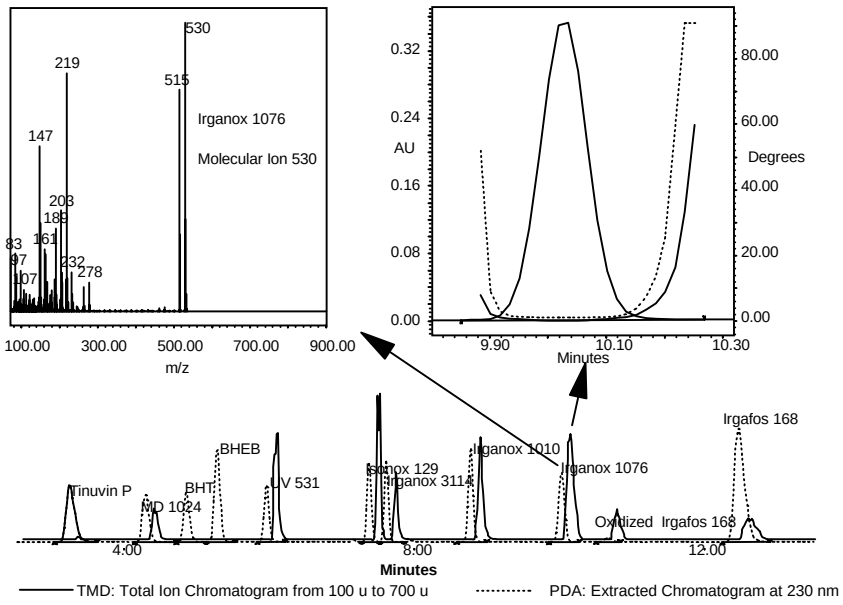
Characterization of Polyolefin Additives by LC/MS

Highlights: Detection and identification of polymer additives leached from polyolefin packaging material by combined PDA /MS detection.

The purpose of this study is to show the feasibility of analyzing polymer additives as well as their degradation products by PDA coupled with Electron Ionization mass detection. A system approach is applied to the identification and confirmation of additives used in the Food Packaging / Medical Device industry. Since polyolefin packaging materials are used extensively in the packaging of food and pharmaceutical products as well as the manufacturing of medical tubing and instrumentation used in surgical procedures, the possibility always exists for small quantities of the additives in the polymeric material to migrate to the surface of the polymer and into the surrounding medium, possibly even into the human body.

An excellent way to characterize these materials is to use reverse phase HPLC coupled with photodiode array detection and mass detection using a particle beam LC/MS interface. Photodiode array detection yields UV spectral information which gives the analyst the ability to determine peak homogeneity. Electron Ionization (EI) mass spectral information coupled with photodiode array information is a powerful tool used to determine positive compound identification.

Additive Analysis Results

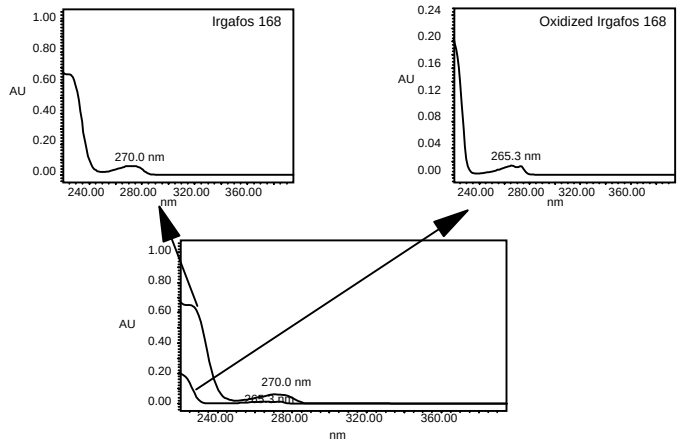


This is an illustration of the multiplicity of data that can be obtained from a single injection on the Integrity system. An overlay chromatogram of the PDA and TMD channels is shown, and since Integrity is a low dispersion system, there is good correlation between the two detectors as well as minimal band broadening through the LC/MS interface. Peak Purity results are also displayed. From PDA data, peak homogeneity as well as linearity and diagnostic information can be obtained. Mass spectra can also be displayed along with chromatography data and PDA results on a single report. Specifically, the mass spectrum of Irganox 1076 is featured here.

Gradient conditions.
Solvent A: Water Solvent B: Acetonitrile Flow rate: 0.6 ml/min
Gradient: 80% to 100% B in 5 minutes hold for 10 minutes
Column: Waters Symmetry C 8 (3.0 mm x 150.0 mm) at 50º C

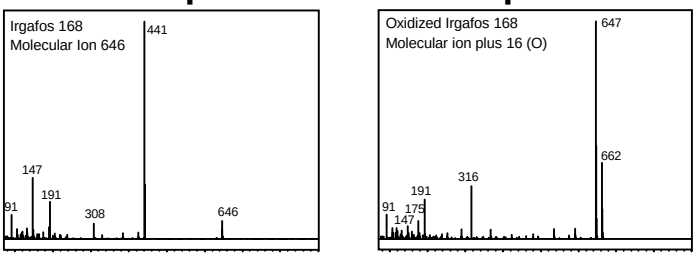
By using the mass detector in combination with the PDA detector, degradation products of various additives can also be identified.

Irgafos 168 and Oxidized Irgafos 168 UV Spectra Comparison

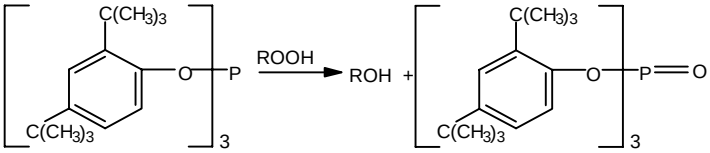


For example, the UV spectrum of Irgafos 168, which is known to under go oxidation, is compared to the UV spectrum of an Irgafos 168 contaminant. It is clear that the two spectra are different, and the PDA library search yielded no useful information about the oxidized Irgafos contaminant.

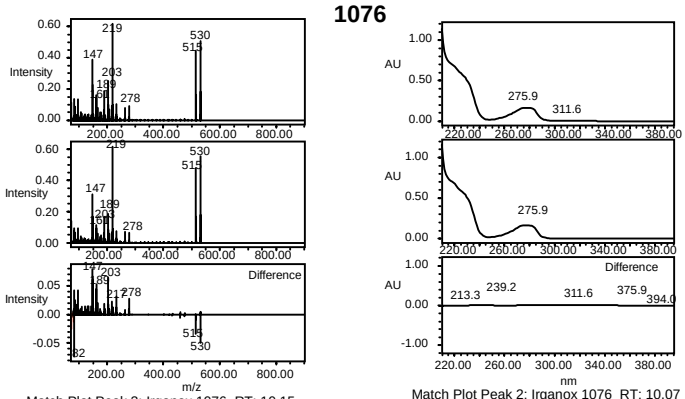
Degradation Product Determination; Comparison of Mass Spectra



The mass spectra, however, were drastically different for the two peaks in the separation. In the case of the Irgafos 168 spectrum, there is a molecular ion at m/z 646, and the compound could easily be identified based on previously run standards. The mass spectrum for the unknown showed what appeared to be a molecular ion at m/z 662 which is 16 mass units higher than the molecular weight of Irgafos 168. This indicates the possibility that the Irgafos was being oxidized.



PDA and TMD User Built Library Search Results for Irganox 1076



Match Plot Peak 3: Irganox 1076 RT: 10.15
Match #1 Fit 94 Irganox 1076

Match Plot Peak 2: Irganox 1076 RT: 10.07
Match #1 Fit 1.121 Irganox 1076

Both PDA and MS spectra are searchable against user built or commercially available (MS only) libraries. This is an example of a library search result for Irganox 1076 from both the PDA and TMD channels. The search results are displayed by Millennium software as "Triple Plots". In the Triple Plot, the top spectrum represents the sample spectrum, the middle spectrum is the library search result spectrum and the bottom spectrum is the difference between the two. In this way, great confidence in positive compound identification of both knowns and unknowns can be achieved.