

The Identification of Polyaromatic Hydrocarbons (PAHs) in a Carbon Black Sample Using the Integrity[™] LC/MS System

Highlights: ThermaBeam[™] Electron Ionization mass spectrometry (TB-EI MS) is utilized for the detection and identification of PAH's in carbon black extracts. The power of combined Photodiode Array (PDA) detection and MS detection, as well as the use of commercial libraries for positive compound identification is discussed.

Carbon black is used heavily in the production of tires and other abrasion-resistant rubber products. It is produced from the burning of heavy oil fractions. The analysis of PAHs in this material has, to this date, not been extensively investigated. However, recent interest in the types of PAHs present in rubber products has increased due to concerns over exposure. Issues regarding the interaction of PAHs in rubber production has also led to the characterization of these compounds in carbon black.

This study utilizes the power of Electron Ionization (EI) mass spectra for the identification of PAHs in carbon black extracts. EI spectra have long been considered to be compound "fingerprints" which can be searched against commercial or user-built data bases, or interpreted for positive compound identification. The Waters Integrity system also generates simultaneous PDA and TB-EI mass spectra for each chromatographic peak in a single injection for greater confidence in peak identification.



A low concentration of a PAH test mix containing sixteen regulated PAH compounds was analyzed on the Integrity system. The two channels of information illustrated above were generated from a single injection. Notice the negligible peak dispersion seen between both detectors. User-built libraries for both PDA and MS data can subsequently be generated from the spectra of these peaks. MS results can also be searched against the Wiley library for compound identification. Copyright 1998 Waters Corporation.





The comparison of the UV and MS chromatograms from a carbon black extract is shown at left. The UV chromatogram (top) is labeled with the peaks identified by a library search against the user built PDA library containing spectra of the 16 PAHs in the EPA mix. An asterisk (*) denotes those peaks that were matched but had been flagged as being spectrally impure (possible coelutions). The bottom chromatogram is the MS plot. Notice that there are several additional peaks here which were not identified by PDA using library search since they do not match any of the sixteen regulated PAHs present in the user built library.

The data below represent the Wiley library search results for further compound identification. Other PAHs in addition to the sixteen mentioned above (Coronene, for example) were identified in the standard by search of their mass spectra against the Wiley Library. Even though there are no UV spectra in the PDA library for these compounds, one can still identify these peaks by MS library search results.

1= Phenanthrene* 2= Fluoranthene *3= Pyrene 4= Benzo(a)pyrene *5= Benzo(g,h,i)perylene 6=Indeno(123-cd)pyrene

* denotes peaks found to be spectrally impure and having high match values.



The TB-EI mass spectra of three of the peaks from the carbon black sample are shown above. Each sample spectrum was searched against the Wiley library for compound identification. The search results are displayed above in a "Triple Plot" format which is a feature in Millennium software that allows for visual comparison of spectra. The Triple Plot compares the "unknown" sample spectrum (top) to the Wiley library match spectrum (center) and shows the difference between the two (bottom). These data show that there is even a good match for the late eluting-Coronene. The Difference plot shows some minor deviations in the low mass region thus explaining the lower match value. This is somewhat expected since the Coronene peak was found by the PDA to be non-homogeneous. An example of the peak homogeneity information generated by the PDA is shown below.

At right is the PDA report for Indeno(1,2,3-cd)pyrene which was found to be homogeneous. This information also shows the user-built PDA library search results. The simultaneous collection of both PDA and MS information is a very powerful technique which leads to greater confidence in peak identification. The determination of peak homogeneity is useful since undetected coelutions produce mixed mass spectra which can interfere with automated library search results and complicate spectral interpretation.

PDA Match and Purity Plot for Indeno (1,2,3-cd)pyrene



The Waters Integrity system combines both PDA and MS detection for a complete picture of the chromatographic peaks in a separation. Positive compound identification of PAHs from a carbon black extract can easily be achieved by seamlessly integrating PDA and MS detection, and the processing and reporting of both types of information. Library search capabilities for both PDA and MS spectra as well as peak homogeneity information also yield valuable data for the identification of unknown or suspected components in a mixture.



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