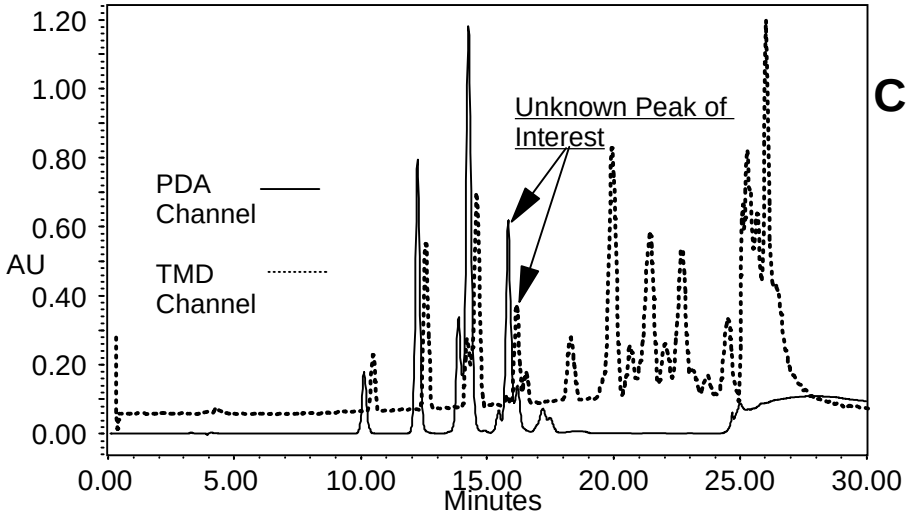
# Waters Integrity System Applications

## Analysis of Fuel Using Combined PDA and MS Detection

**Highlights:** The use of Photodiode Array detection coupled with a ThermaBeam LC/MS interface for the characterization and analysis of oil by-products (fuels) is investigated.

Typically, oils have been difficult to analyze due to their complex nature. Previous analysis involved breaking down oil samples into fractions using preparative chromatography or distillation. These fractions were then further characterized in order to determine the chemical makeup of the oil. The development of new LC/MS interfaces as well as improvements in HPLC and column chemistry have greatly assisted in the characterization of the various components in heavy oils. This study featuring the Integrity LC/MS System, combines photodiode array (PDA) detection and mass spec (MS) detection using a ThermaBeam interface in order to identify an unknown component found in a White Gas sample. The ThermaBeam LC/MS interface used with Electron Ionization (EI) yields reproducible, interpretable and library searchable EI spectra which are used to identify unknown components in a mixture. PDA detection provides UV separation monitoring as well as peak homogeneity information. The combined data from simultaneous UV and MS detection obtained from a single sample injection is a powerful technique for absolute compound identification.

**Analytical Conditions:**
Waters Symmetry C18 Column (3.9 X 150mm)
Gradient Conditions: Reverse phase separation using:
Solvent A: Water
Solvent B: Acetonitrile
Solvent C: THF
Flow Rate: 0.5 ml/min
50 % A for 2 min. to 100 % B in 15 min. Hold for 5 min. Then step to 100% C. Hold for 10 min.

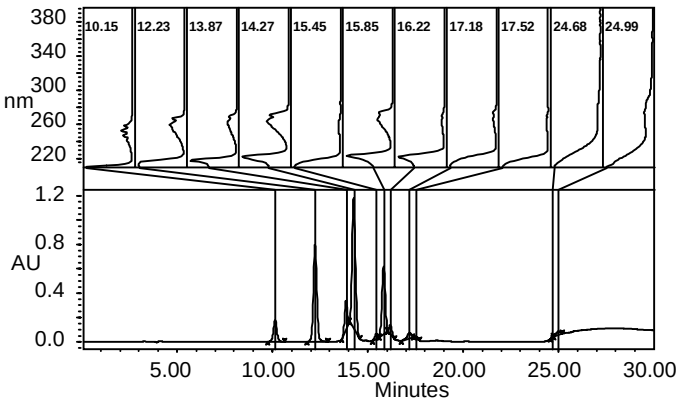



## PDA and MS Overlay Chromatograms of a White Gas Sample

The overlay of the PDA and the MS chromatograms acquired from a single sample injection is shown at right. The Integrity LC/MS System has the capability to directly compare data from both channels so that greater confidence in peak identification can be achieved. Note the unknown peak of interest. This study will illustrate the use of both PDA and MS data in the identification of this peak.

# PDA Spectrum Index Plot

Fig. A.




# TMD Spectrum Index Plot

**(0 to 21 min.)**

Fig. B.

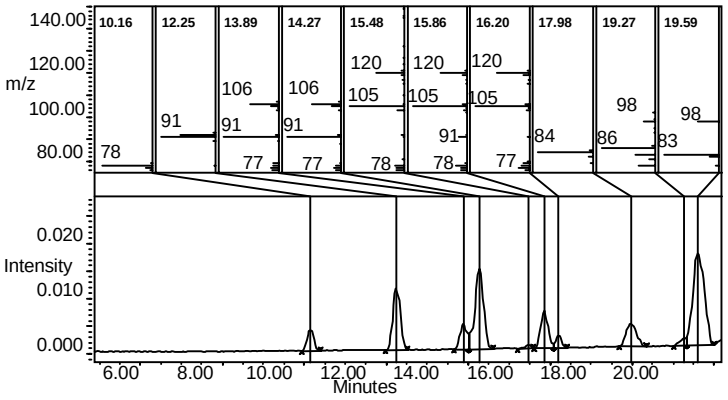
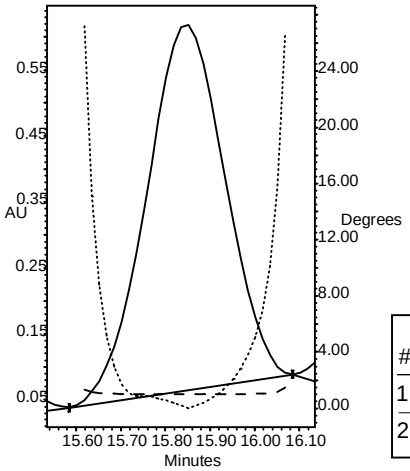



Figure A shows the PDA Spectrum Index Plot for the White Gas sample, while Figure B shows the MS Spectrum Index Plot. The Integrity System's Millennium software has the unique ability to display either UV spectra or MS spectra above chromatographic peaks. In this way, a visual comparison of spectra within a chromatogram for both channels of information is possible. For the unknown peak at 15.86 minutes, both the UV spectrum and the mass spectrum can be directly compared for peak identification. Figure C. shows peak purity information obtained from the PDA which can be used to determine peak homogeneity. PDA spectra can also be matched against a user created library for identification purposes. Figure D. shows the MS library search results of a spectrum from the unknown peak matched against the Wiley library. The Triple Plot illustrates the unknown spectrum, the library match spectrum and the difference between the two spectra. Notice the "Fit" and "% Contamination" values for the match. These numbers confirm the likelihood that the identification of the unknown peak as 1,2,4-trimethyl benzene is reasonable.

Positive compound identification of unknown materials in fuel samples is easily achieved using the Waters Integrity LC/MS System. Simultaneous acquisition of PDA and MS data on a single injection and seamless processing and reporting of both channels of data as well as automated library search capabilities offer confidence in peak identification.




# Unknown Peak Purity Information

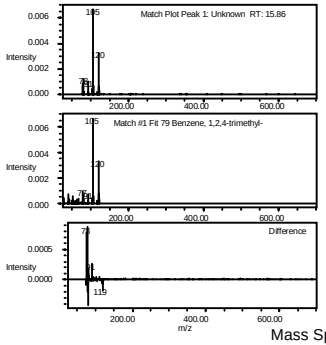
Fig C.

Purity Pass #1 ------

Noise + Solvent (1.00) – –

Peak Purity Passes Table

| # | Purity Angle | Purity Threshold | Purity Flag | Maximum Impurity |
|---|---|---|---|---|
| 1 | 1.121 | 1.007 | * | 15.968 |
| 2 | 0.649 | 1.007 | | 15.768 |




# Unknown Peak Library Match Results

Fig D.

Mass Spec Match Results

| # | PBM Fit | Percent Contamination | Spectrum Name | Library Name | Molecular Weight | Formula | CAS Number |
|---|---|---|---|---|---|---|---|
| 1 | 79 | 22 | Benzene, 1,2,4-trimethyl- | WILEY | 120 | C9 H12 | 95-63-6 |
| 2 | 67 | 26 | 3-ETHYLTOLUENE | WILEY | 120 | C9 H12 | 0-00-0 |
| 3 | 67 | 26 | Benzene, 1,2,3-trimethyl- | WILEY | 120 | C9 H12 | 526-73-8 |