IRD 3 Application Note

PNA Ring Isomers

Introduction

While the mass spectrometer produces powerful structural information based on molecular fragmentation, often including molecular weight data, MS can be weak differentiating polynuclear aromatic hydrocarbons (PNA) ring bonding. Conversely, the infrared spectrometer is strong in these areas.

This note highlights the power of the IRD 3 to aid in the distinguishing of the some polynuclear aromatic hydrocarbons. While this example is chosen from the area of industrial chemistry, knowledge of PNA ring bonding has broad applicability in all area where structural identification is important.

The PNAs are naturally present in fossil and synthetic fuels, and can be formed during incomplete combustion of these fuels. PNAs have been found in diesel exhaust, wood smoke, coal, coal liquefaction and gasification products, creosote, and oil shale. From a health and environmental standpoint, the mutagenic and carcinogenic properties of the some PNAs are of concern. The PNAs were one the earliest compound classes to be shown as carcinogenic from the studies of chimney sweeps and coke-oven workers. The carcinogenic and mutagenic activity apparently stems from the oxidation products of the PNAs. Thus controlling emissions and site characterization and remediation are of great importance.

Product Overview

The IRD 3 is designed from the chromatographer's point-of-view and is the only analytical infrared instrument that seamlessly combines the separating power of the Gas Chromatography with the molecular identification of FTIR.

- Dedicated FTIR for use with GC
- Low maintenance and easy to use
- Small footprint
- Software interfaces with GC control software
- Seamless integration with MS

The IRD 3 is the perfect tool for the chromatographer looking to obtain more information about unknown samples. Using a heater light pipe flow cell, the sample is kept in a vapor state while interacting with IR. This allows the molecules to freely rotate in a low energy environment. Keeping the molecular geometry in tack during analysis provides unique and highly reproducible spectra.

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Parameters and Result

Polynuclear aromatic condensed ring compounds absorb in the same general regions as benzene derivatives, with the carbon-hydrogen stretching vibrations at 3030 to 3100cm-1 and the with out-of-plane deformations occurring from 675 to 900cm-1. Specifically, these deformations are as follows: one isolated aromatic hydrogen atom, 830 to 900cm-1; two adjacent aromatic hydrogen atoms, 810 to 850cm-1; three adjacent aromatic hydrogen atoms, 730 to 760cm-1 and 785 to 815cm-1; and four adjacent aromatic hydrogen atoms, 740 to 770cm-1. Out of plan ring vibrations occur at wavenumbers less than 500.

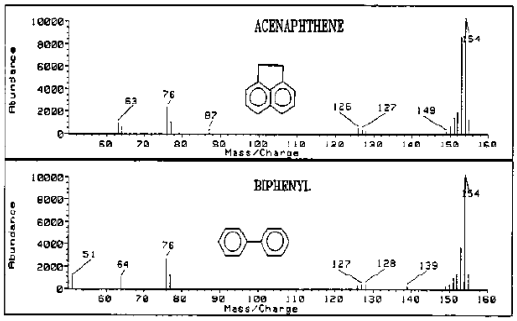

Figure 1. Mass spectra of acenaphthene and biphenyl

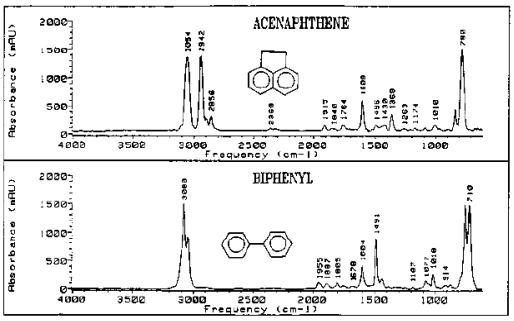

Figure 2. Infrared spectra of acenaphthene and biphenyl

As can be seen in the figure 1, mass spectra of PNAs give strong molecular ions and little definitive fragmentation information. This leads to considerable uncertainty in making identifications based on mass spectral information alone. However, the infrared spectra (figure 2) of PNAs of the same molecular weight are different and identifications can easily be made based on infrared data.

PBM library searches of the NBS or the Wiley mass spectral libraries cannot differentiate between anthracene and phenanthrene. This is understandable when one examines their mass spectra, see Figure 3. Their infrared spectra, see Figure 4, are entirely different and a search of the EPA Vapor Phase Library easily tells them apart. In order to achieve a very high confidence determination, a combined IR and MS library search was performed.

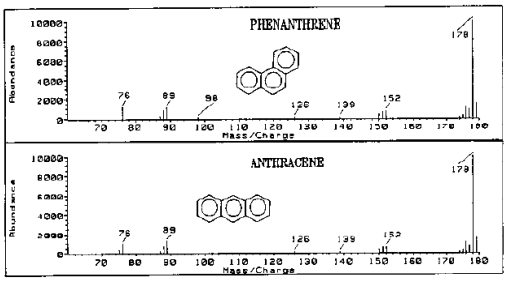

Figure 3. Mass spectra of phenanthrene and anthracene

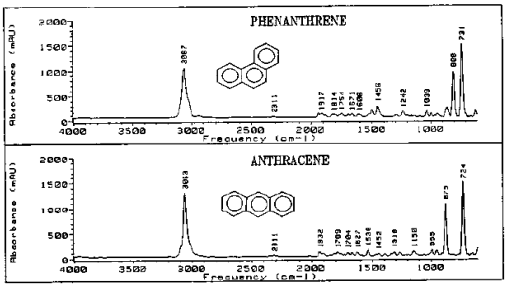

Figure 4. Infrared spectra of phenanthrene and anthracene

Conclusion

The GC-IRD has been shown to be useful in the differentiation of similar polynuclear aromatic hydrocarbons, specifically in this example of phenanthrene and anthracene. The combined IRD and MSD provide higher confidence results than either technique alone.

Method Parameters

Gas Chromatograph
Column: 50m HP 5 (5% phenyl – methylsilicone), 0.32mm id x .52um film
Carrier Gas: Helium at 1.4mL/min
Oven: 34°C (10 min) to 140°C at 5°C/min
Injection Port: 250oC
Sample Injection: 1ul, split 30 to 1
IRD Parameters
Light Pipe: 250°C
Transfer Lines: 250°C
Resolution: 8cm^{-1}
Detector: Wide Band MCT, 4000-550cm^{-1}
MSD Parameters
Transfer Lines: 280°C