HEWLETT PACKARD

The Power of the IRD: Polynuclear Aromatic Hydrocarbon Ring Bonding

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IRD Application Brief

HP 5965B IRD
Infrared Detector

IRD90-1

IRD Productivity Profile

Industry
Industrial chemical
Environmental

Chemicals
Acenaphthene, biphenyl, phenanthrene, anthracene, fluoranthene, pyrene

Sample Matrix
Reaction mixtures, products, residues

Analysis
Structural Identification

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 hydrocarbon (PNA) ring bonding. Conversly, the infrared spectrometer is strong in these areas.

This note highlights the power of the HP 5965B IRD to aid in the distinguishing of 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 areas where structural identification is important.

Sample Background

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 liquifaction and gasification products, creosote, and oil shale. From a health and environmental standpoint the mutagenic and carcinogenic properties of some PNAs are of concern. The PNAs were one of the earliest compound classes to be shown as carcinogenic from the studies of chimney sweeps and coke-oven workers. This 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.

Spectral Studies

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

As can be seen in the figures, 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 of PNAs of the same molecular weight are different and identifications can easily be made based on infrared data.

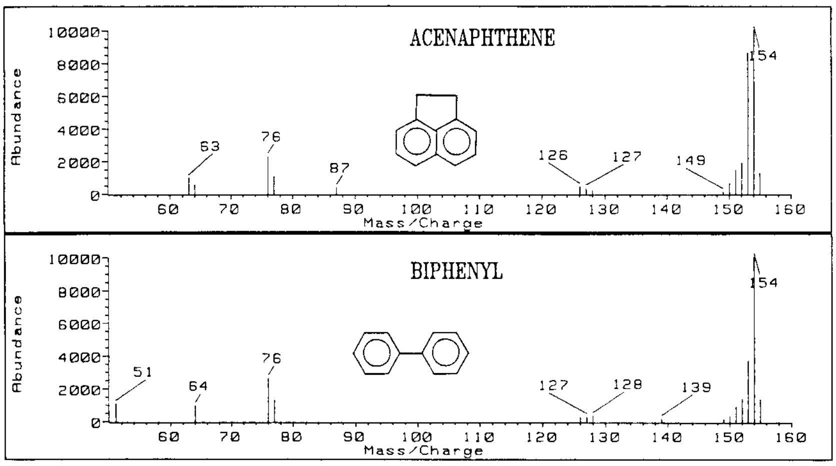

Figure 1. Mass spectra of acenaphthene and biphenyl

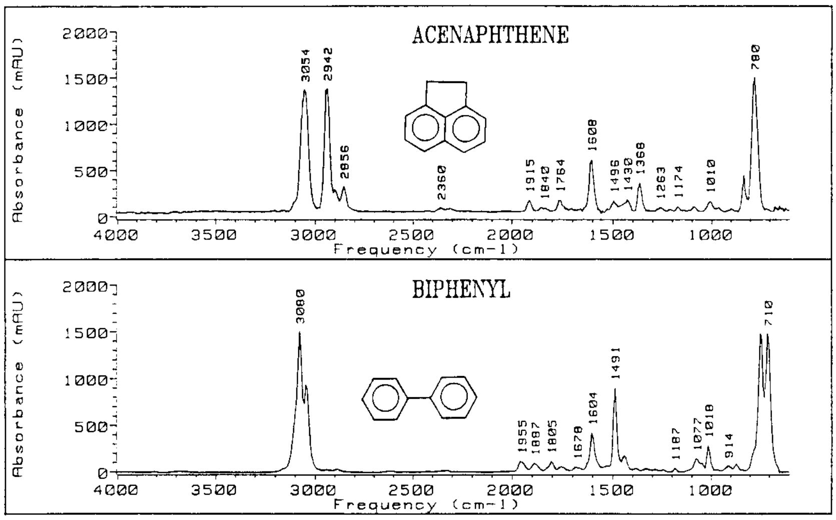

Figure 2. Infrared spectra of acenaphthene and biphenyl

High Confidence Determination

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 IR Library easily tells them apart. In order to achieve a very high confidence determination, a combined IR and MS library search was performed. As an example of this, see Figure 7, where phenanthrene was found. Note that phenanthrene is the only Class 1 hit, i.e., it was on both the IR and MS hit lists. Anthracene, with the same PBM match quality index as phenanthrene, gave a Class 3 hit, i.e., the compound is in both libraries but never even appeared on the IR hit list. Clearly the IRD and its combined IR and MS searching capability gives a high confidence qualitative solution. Similar combined search results are obtained with acenaphthene–biphenyl and fluoranthene–pyrene.

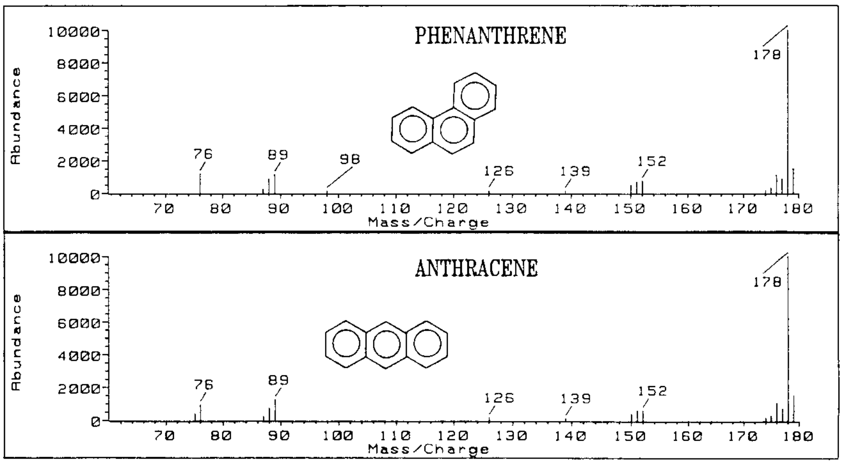

Figure 3. Mass spectra of phenanthrene and anthracene

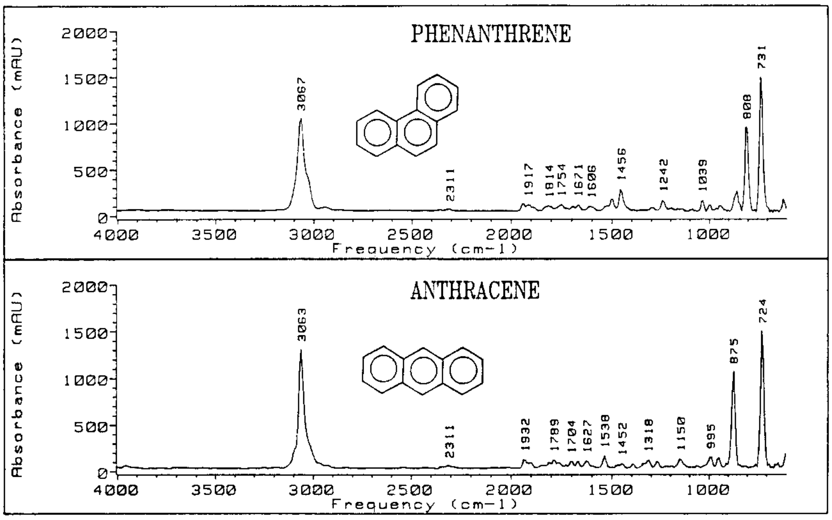

Figure 4. Infrared spectra of phenanthrene and anthracene

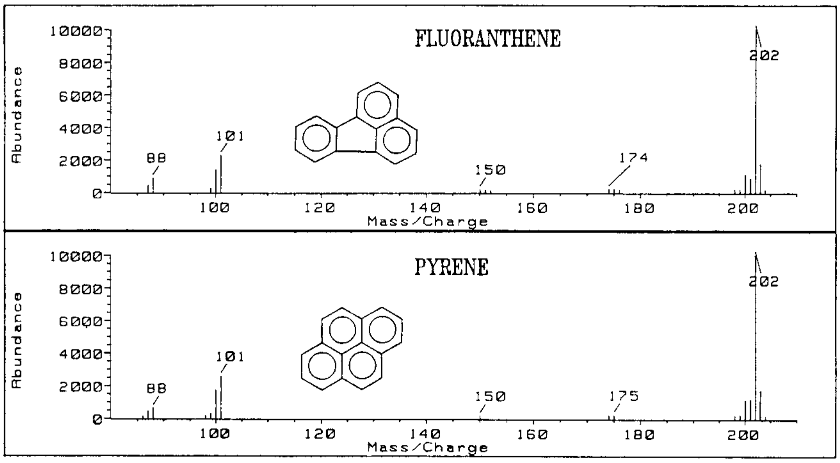

Figure 5. Mass spectra of fluoranthene and pyrene

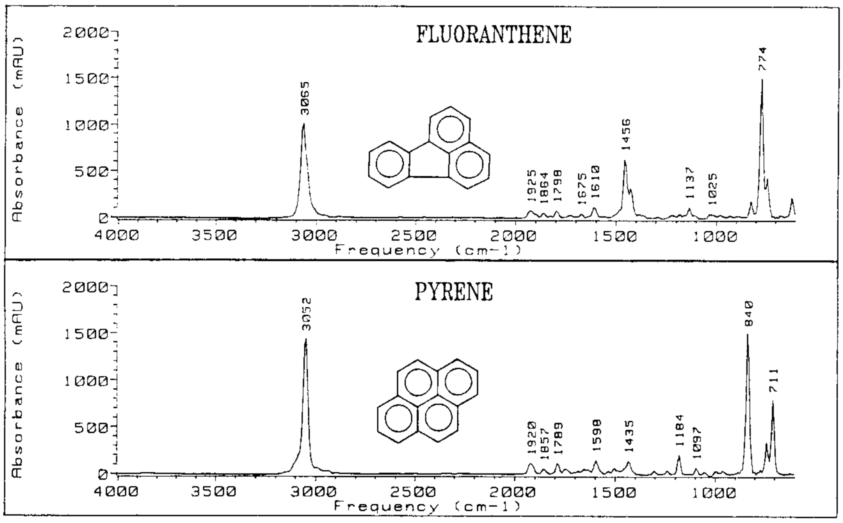

Figure 6. Infrared spectra of fluoranthene and pyrene

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.

Conditions

IRD Parameters

Flow Cell 280°C

Optical resolution 8 cm^{-1}; wide band MCT detector

COMPARISON OF RESULTS FROM

PBM Search of Library file: DATA:NBS43K.L
Avg 14.622:14.793 min. from DATA:PNASTDMS.D
PNA SAMPLE

AND

IR Search of Library file: DATA:EPA_REVA.L
Avg 14.622:14.793 min. from DATA:PNASTDMS.D
PNA SAMPLE

Class 1 (on both lists)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
1.	000085-01-8	96	984	178	C14H10	Phenanthrene (8CI9CI)

Class 2 (in only one library)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
2.	004425-82-5	91	---	178	C14H10	9H-Fluorene, 9-methylene- (9CI)
3.	000886-38-4	72	---	206	C15H10O	2-Cyclopropen-1-one, 2,3-dipheny
4.	000501-65-5	72	---	178	C14H10	Benzene, 1,1'-(1,2-ethynediyl)bi
5.	054549-75-6	50	---	178	C10H10O3	1(2H)-Naphthalenone, 3,4-dihydro
6.	012129-51-0	38	---	234	C12H10O2Ti	Titanium, dicarbonylbis(.eta.5-2
7.	054966-09-5	37	---	178	C10H14N2O	1-Piperidinecarboxaldehyde, 2-(1
8.	002524-67-6	37	---	178	C10H14N2O	Benzenamine, 4-(4-morpholinyl)-
9.	019064-68-7	33	---	178	C9H7ClN2	Phthalazine, 1-chloro-4-methyl-
10.	000531-75-9	33	---	340	C15H16O9	2H-1-Benzopyran-2-one, 6-(.beta.
11.	001202-62-6	28	---	178	C10H14N2O	Methanimidamide, N'-(4-methoxyph
12.	001485-07-0	---	890	172	C12H12O	2-NAPHTHALENEETHANOL
13.	005859-45-0	---	884	176	C11H9Cl	NAPHTHALENE, 1-CHLORO-2-METHYL

Class 3 (in both libraries, but on only one list)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
14.	000120-12-7	96	---	178	C14H10	Anthracene (8CI9CI)
15.	000091-57-6	---	916	142	C11H10	NAPHTHALENE, 2-METHYL
16.	000098-07-7	---	903	194	C7H5Cl3	TOLUENE, A,A,A-TRICHLORO
17.	000119-64-2	---	895	132	C10H12	NAPHTHALENE, 1,2,3,4-TETRAHYDRO
18.	000939-27-5	---	894	156	C12H12	NAPHTHALENE, 2-ETHYL
19.	000091-22-5	---	890	129	C9H7N	1-BENZAZINE
20.	000102-46-5	---	882	154	C9H11Cl	BENZENE, 4-/CHLOROMETHYL/-1,2-DI
21.	002586-62-1	---	881	220	C11H9Br	NAPHTHALENE, 1-BROMO-2-METHYL

Figure 7. Combined IRD and MSD library search results for phenanthrene