
Characterization of a synthetic jet engine lubricating oil by combined GC/FTIR/MS and GC/AED

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IRD Application Note

**HP 5965B, HP 5971A
HP 5921A**

IRD 92-1

IRD productivity profile

Industry

Petroleum, Petrochemical

Chemicals

Long chain esters
Tricresyl phosphates
Antioxidants

Analysis

Identification of Components

Abstract

A synthetic jet engine lubricating oil was examined using GC/AED to screen for the elements present and GC/IRD/MSD to identify the components.

Introduction

Synthetic lubricating oils have been developed to meet the increasing demands of advancing technology or previously as substitutes for wartime generated petroleum shortages. While natural petroleum oils augmented with additives are generally quite satisfactory, for severe requirements more controllable synthetic materials with superior properties may be called for. This is true not only of the main lubricating agent, but of the antioxidants and detergents as well.

Because of the complex nature of lubricating oils, it is often very difficult to identify and quantitate important compounds in them. The analysis of additives, for example, is usually hampered by severe chromatographic overlap with the base oil components.

A new analytical approach using GC/AED, GC/IR, and GC/MS is used here to find the additives in a commercial jet engine oil. The analytical scheme for component identification can be summarized as listed on the next page.

1. Run the sample on GC/AED to produce a series of element selective chromatograms. These chromatograms will indicate the elements that are present (and those which are absent) in the chromatogram. Note the element content indicated for each peak in the chromatogram. This element screening can be used to prioritize which peak to identify first. If chlorine compounds are of special interest, they can be found and worked on first.
2. Run the sample on combined GC/IR/MS. The IR data is first plotted as series of selected wavenumber chromatograms (SWCs) chosen to reflect any functional groups that could be present. These include aliphatic, aromatic, unsaturated, hydroxyl, carbonyl, ether, ester, nitro, amine, and other functionality. This information is used to note the functional group content of each GC peak. At this point, from the AED and IR data, we can now say that a given peak is, for example, an aromatic chloro ether.
3. From the MS data, plot extracted ion chromatograms, for any ions of interest. These can be used to screen for structures like methyl esters, monosubstituted benzenes, tricresyl phosphates, etc. They can also be used to

screen for a particular compound using the molecular ion of that compound. These plots are then used to determine further information about each peak. At this point we now can say that a given peak is, for example, a chloro disubstituted benzene ether with an aliphatic side chain.

4. The last step is to run MS and IR library searches for the peaks of interest. In many cases the compounds will be identified directly from this search process. However, there are many times when library searching fails to provide for the correct identification due to the absence of the compound from the library, spectral overlap, spectral similarities, etc. In these cases the dossier of information obtained by steps 1–3 above can be used to choose between ambiguous library search results, or at least give some data on peaks which are absent from the library. At the very least, for a compound that cannot be identified, we can say that it is, for example, a chloro disubstituted benzene ether with an aliphatic side chain that has a probable molecular weight of 196.

The power of this approach is illustrated in the following analysis of additives in a commercial jet engine oil.

Hardware

For the GC/IRD/MSD system, the gas chromatograph, an HP 5890A was set up using a fairly short intermediate film thickness methyl silicone column programmed to a high (300°C) temperature for complete elution of the heavier components. The column effluent was split at the end of the column at a 10 to 1 ratio with the bulk of the flow going to the HP 5965B IRD and the lesser amount going to the HP 5971A MSD. The details of this parallel configuration are described elsewhere (1,2).

For the GC/AED system, the gas chromatograph an HP 5890A was set up using a fairly short thin film Megabore column under similar GC conditions. Details of the design and operation of the HP 5921A Atomic Emission Detector are covered elsewhere (3,4).

Results

Element screen with Atomic Emission Detector

Figure 1 shows six of the ten element chromatograms obtained with the AED. These chromatograms show that the base stock of the oil is not hydrocarbon in nature but is an oxygenated base, as can be seen in the C, H, and O chromatograms. Also apparent is the presence of two nitrogen compounds and a group of phosphorous compounds, all of which are probably additives. The silicon channel is included as an example to

show what elements are absent. Also absent were Zn, Cl, F, and Br compounds.

Functional group screen with IRD

Figure 2 shows the MS Total Ion Chromatogram (TIC) and the IRD Total Response Chromatogram (TRC) for the sample. Comparison with the AED chromatograms allows correlation of the retention times. Also in Figure 2 is the SWC for esters. Note that we now know that the base stock consists of esters.

Figure 3 shows the aromatic SWC from the IRD screen. Note this contains a wealth of information. First we see that the base stock is not an aromatic ester. Second, it appears that both of the nitrogen containing compounds, as well as all of the phosphorous compounds found with the AED, are aromatic. Also in Figure 3 is the SWC corresponding to the P-O-C functional group. We know at this point that these phosphorous compounds are aromatic with a P-O-C linkage.

Extracted ion screen with MSD

Based on the above results, it was suspected that the group of phosphorous compounds contained tricresyl phosphates (TCPs). Also in Figure 3 is the extracted ion profile from the MS data for m/z 368, which is the characteristic molecular ion for the TCPs. As is clear from Figure 3, the largest phosphorous peaks are indeed TCPs.

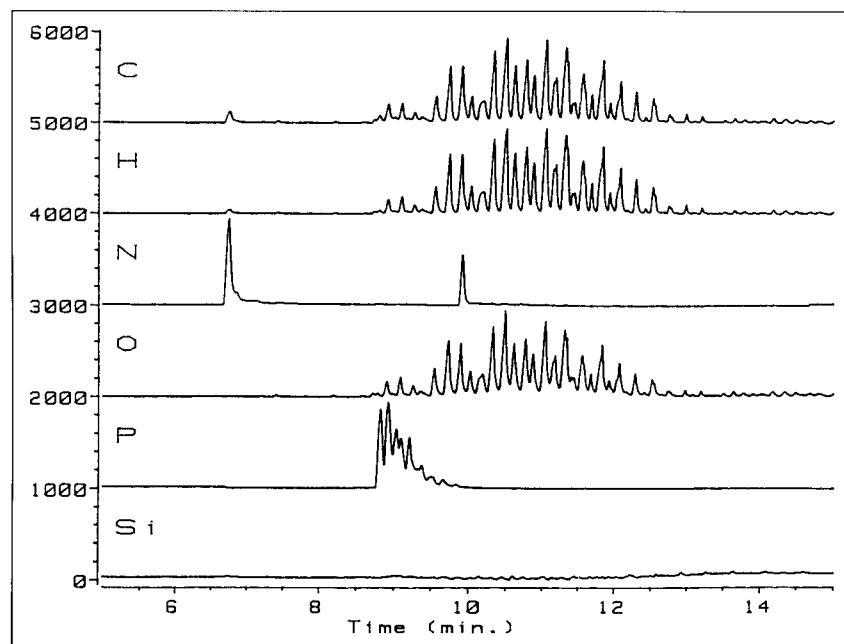


Figure 1. Element specific chromatograms for synthetic jet engine lubricating oil: carbon, hydrogen, nitrogen, oxygen, phosphorus, and silicon

At this point, the screening process (steps 1–3) has told us that the base oil is a non-aromatic ester base. It has also told us that the main additives are two aromatic nitrogen compounds and a group of tricresyl phosphates. The next step is to use the library search routines to identify these compounds.

Library searches

The library searches were performed using the 54000 entry NIST MS library and the 5200 entry Aldrich Vapor Phase IR Library. One of the features of the IR software is that of combining library search results. This produces a hit list merged by common CAS Registry num-

bers into three categories. Class 1 contains those entries which are on both hit lists. Class 2 contains those entries which fall on only one list because the entry is not present in the other library. Class 3 consists of those entries which are in both libraries, but showed up in only one of the two hit lists.

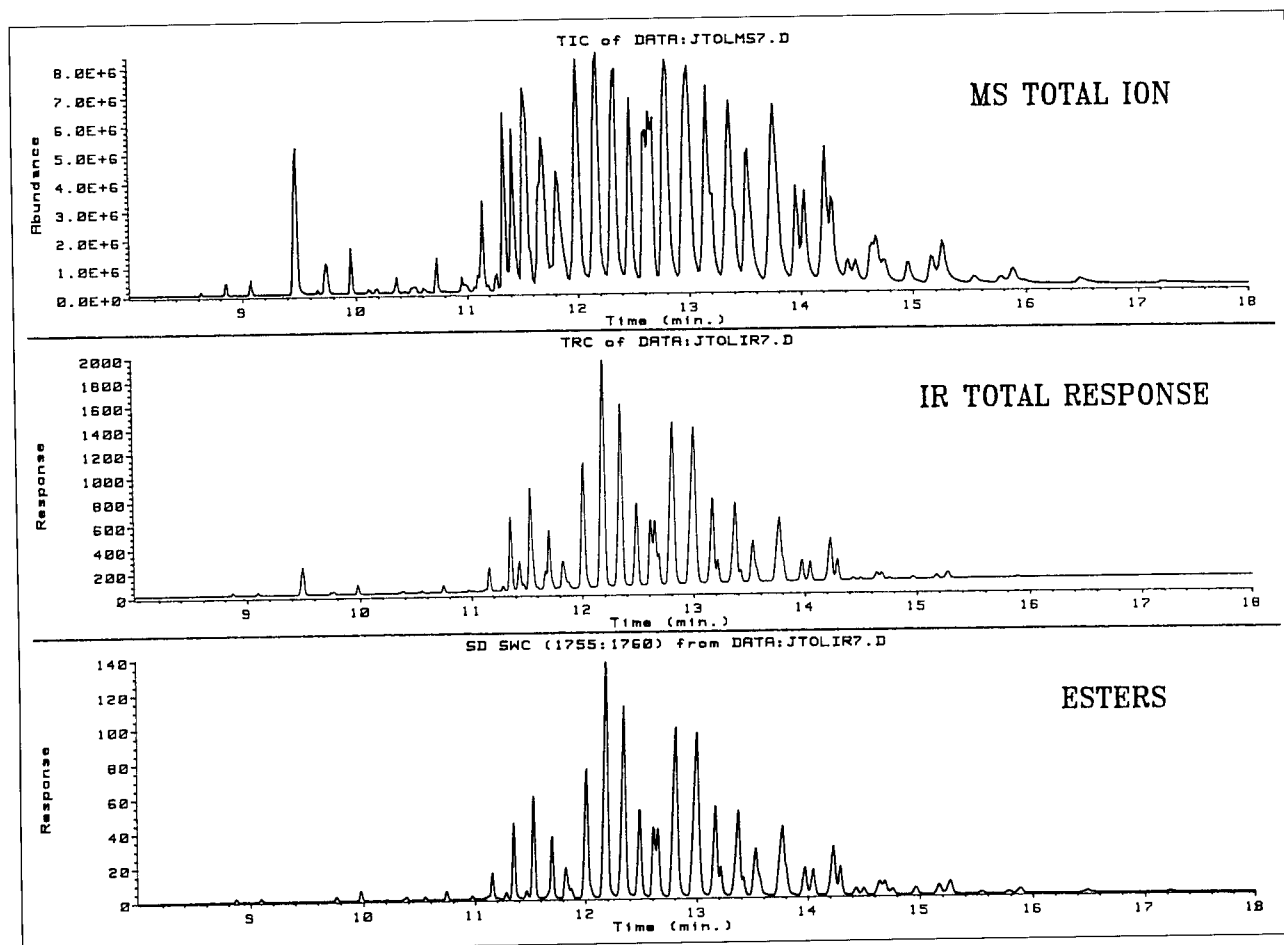


Figure 2. TIC, TRC, and Selected Wavenumber Chromatograms. SWC for ester range of 1755 to 1760 cm^{-1}

Aromatic nitrogen additives

The infrared and mass spectra of the first aromatic nitrogen additive at 9.4 minutes is shown in Figure 4. Examination of these spectra indicate an aromatic amine, exactly in line with the AED and IRD screening results.

Figure 5 shows the combined library search results for the peak at 9.4 minutes. In this case, the Class 1 hits are both N-phenyl-naphthalene amines

with the 1-isomer (Nonox-A) the top hit in both IR and MS. When comparing the IR and MS library searches, this type of entry has a very high probability of correctly identifying the unknown. Taken with the corroboration of the screening results from AED and IRD, there is very high confidence in this peak being Nonox-A.

Note that there are several monosubstituted naphthalenes on the IR hit lists. Isomers, because of their nearly identical

mass spectra, often only appear on the MS hit list. Homologous series, on the other hand, because of their spectral similarities, only appear on the IR hit list. If the IR spectrum of a specific unknown compound is not in the library, typically the near misses are of the same chemical class. This is a very powerful feature of infrared spectroscopy which can be favorably exploited.

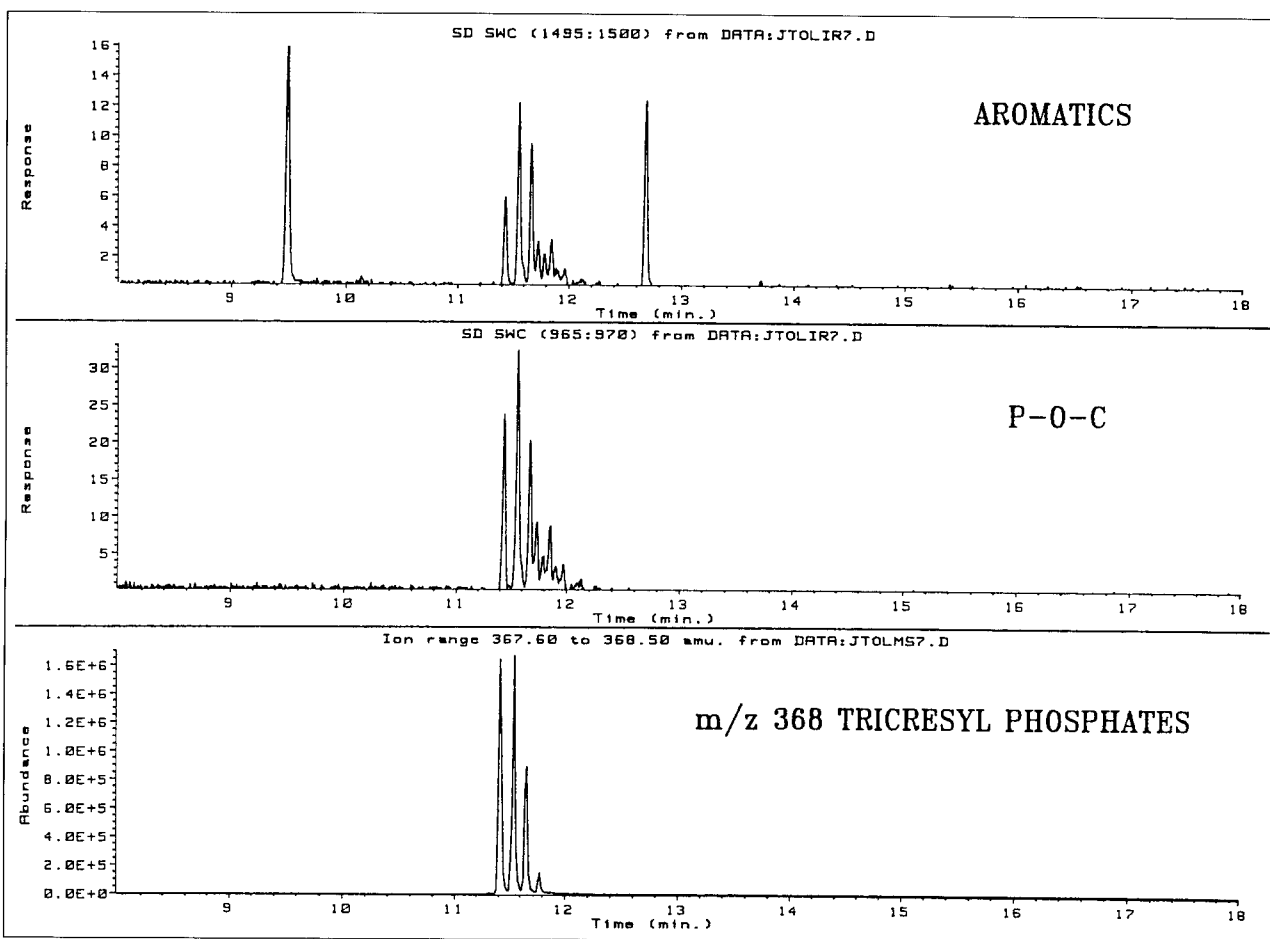


Figure 3. Chromatographic simplification through the use of Selected Wavenumber and Extracted Ion Chromatograms

The infrared and mass spectra of the second aromatic nitrogen additive found in the screen are shown in Figure 6. This compound was not present in either library. We do, however, know from the data that it is aromatic, contains amine nitrogen, has an odd number of nitrogens, contains ca. 32 carbons and has a probable molecular weight of 393. This information is very useful if spectral interpretation is used in an attempt to identify the peak.

TCP additives

Figure 7 shows the infrared and mass spectra of the first peak in the TCP group at 11.4 minutes. The MS library search confirmed that the compound was a TCP, but gave no clue as to which isomer it was. IR, which is much better at distinguishing between positional isomers, confirmed that the peak is trimeta cresyl phosphate. More GC/IR/MS details of TCPs are available in an Applications Brief on hydraulic oil additives (5).

Base oil esters

Long chain diesters are commonly used as synthetic lubricants. Figure 8 shows the infrared and mass spectra of one of the base oil ester peaks at 11.3 minutes. The mass spectrum indicates a long chain ester with a likely molecular weight 444, while the infrared spectrum indicates a long chain aliphatic ester as well. Figure 9 gives the library search results for this peak. Clearly the compound is not in either library. Similar negative results were found for the other esters.

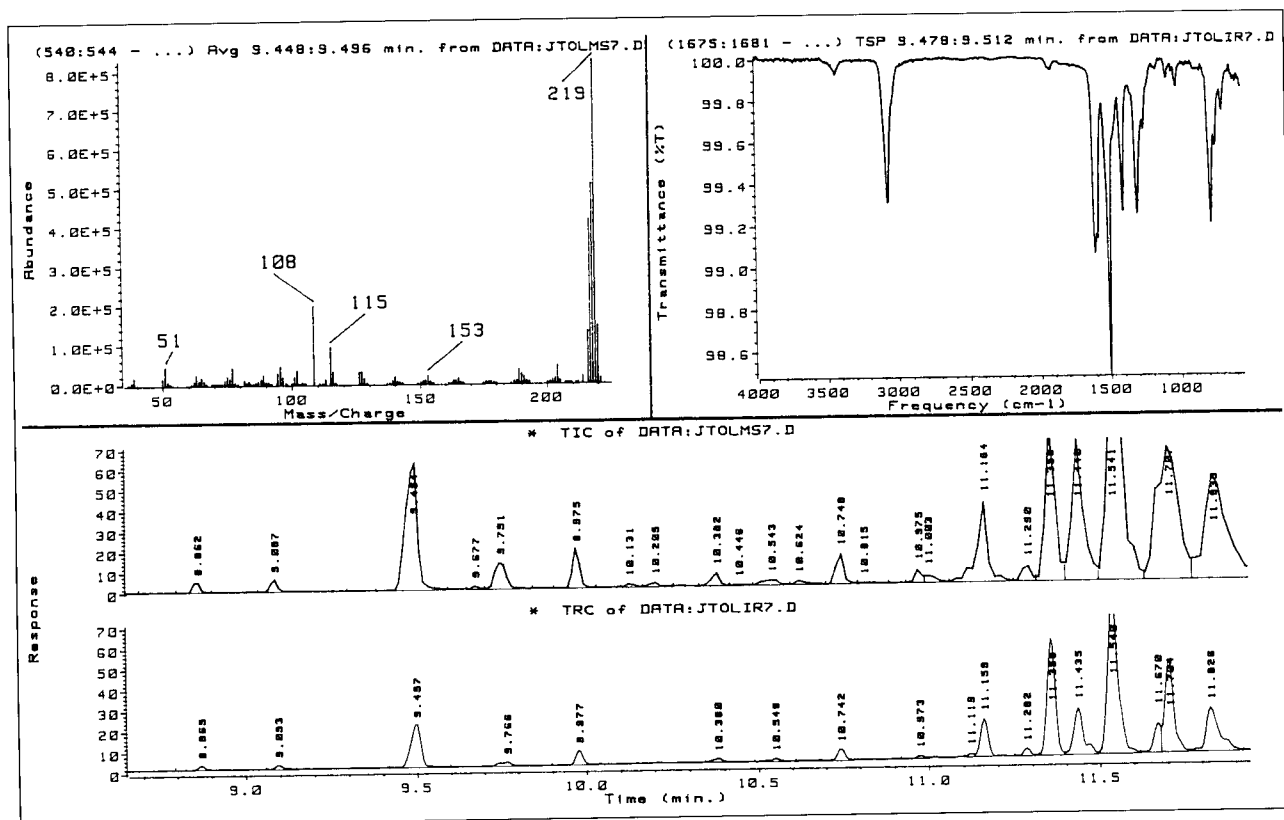


Figure 4. Combined display of peak at 9.4 minutes showing mass and infrared spectra and a portion of the TIC and TRC

COMPARISON OF RESULTS FROM

PBM Search of Library file: DATA:NBS54K.L
Avg 9.448:9.496 min. from DATA:JTOLMS7.D

AND

IR Search of Library file: DATA:ALDRICH.L
RSP 9.478:9.512 min. from DATA:JTOLIR7.D
JET ENGINE OIL

Class 1 (on both lists)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
1.	000090-30-2	93	972	219	C16H13N	1-Naphthalenamine, N-phenyl-
2.	000135-86-6	53	913	219	C16H13N	2-Naphthalenamine, N-phenyl-

Class 2 (in only one library)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
3.	055028-73-4	38	---	218	C17H14	1,4-Methanonaphthalene, 1,4-dihy
4.	003274-56-4	35	---	219	C16H13N	1H-Pyrrole, 2,4-diphenyl-
5.	000613-59-2	32	---	218	C17H14	Naphthalene, 2-(phenylmethyl)-
6.	004789-76-8	28	---	219	C16H13N	Quinoline, 4-methyl-2-phenyl-
7.	054884-99-0	17	---	219	C16H13N	6-Benzylquinoline
8.	028748-19-8	17	---	219	C16H13N	8-Benzylquinoline
9.	028748-14-3	17	---	219	C16H13N	5-Benzylquinoline
10.	034777-33-8	12	---	217	C16H11N	Benzo(c)carbazole
11.	000239-01-0	10	---	217	C16H11N	11H-Benzo(A)carbazole
12.	039227-54-8	9	---	218	C12H7ClO2	Dibenzo[b,e][1,4]dioxin, 2-chlor
13.	000243-51-6	8	---	217	C16H11N	11H-Indeno(1,2-B)quinoline
14.	000624-31-7	7	---	218	C7H7I	Benzene, 1-iodo-4-methyl-
15.	000243-42-5	7	---	218	C16H10O	Benzo[b]naphtho[2,3-d]furan
16.	001205-64-7	---	916	183	C13H13N	3-METHYLDIPHENYLAMINE, 98%
17.	000101-17-7	---	906	204	C12H10ClN	3-CHLORODIPHENYLAMINE, 99%
18.	003163-27-7	---	882	221	C11H9Br	1-(BROMOMETHYL)NAPHTHALENE, 98%

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

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
19.	000625-95-6	10	---	218	C7H7I	Benzene, 1-iodo-3-methyl-
20.	000615-37-2	10	---	218	C7H7I	Benzene, 1-iodo-2-methyl-
21.	002693-46-1	10	---	217	C16H11N	3-Fluoranthenamine
22.	000122-39-4	---	915	169	C12H11N	DIPHENYLAMINE, 99+%, A.C.S. REAG
23.	000090-12-0	---	894	142	C11H10	1-METHYLNAPHTHALENE, 98%
24.	001127-76-0	---	886	156	C12H12	1-ETHYLNAPHTHALENE, 99+%
25.	000605-02-7	---	885	204	C16H12	1-PHENYLNAPHTHALENE, 96%
26.	000321-38-0	---	869	146	C10H7F	1-FLUORONAPHTHALENE, 99%

Figure 5. Combined library search results for peak at 9.4 minutes indicating N-phenyl-1-naphthylamine (Nonox A)

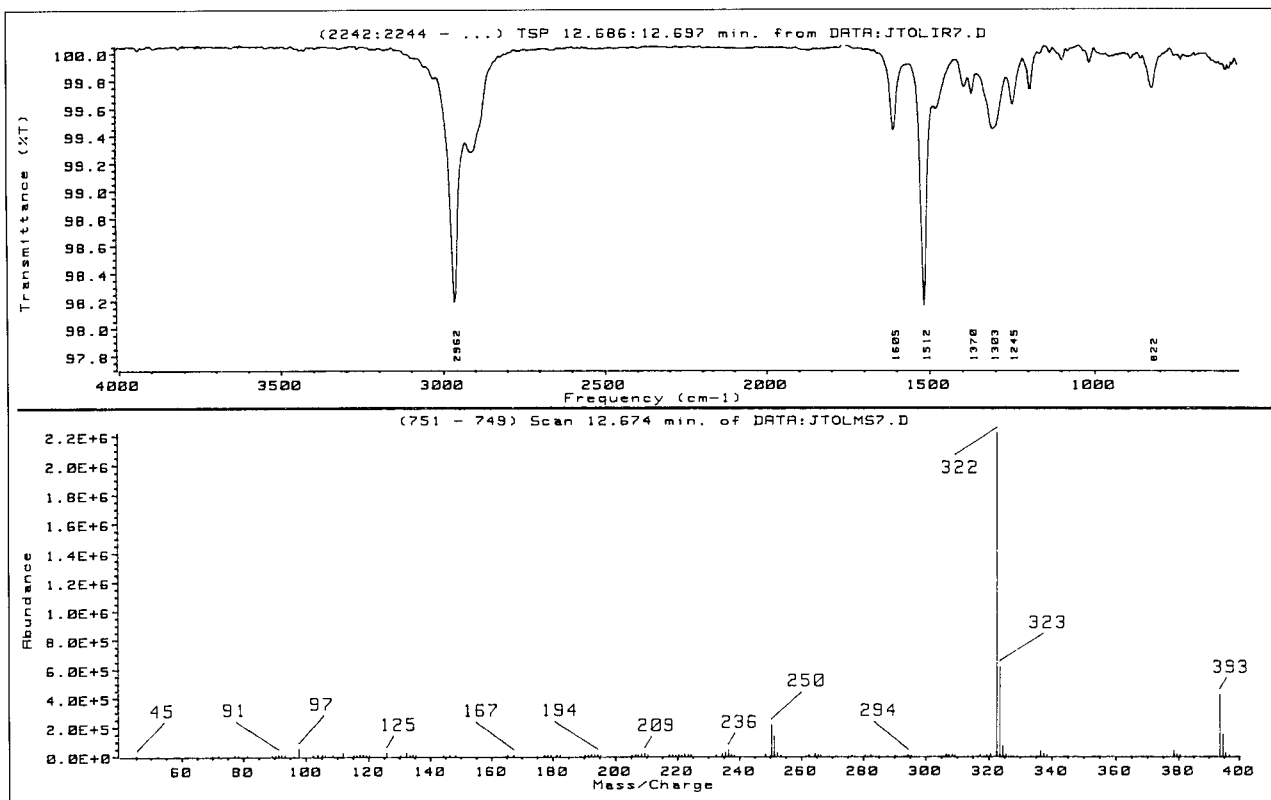


Figure 6. Infrared and mass spectra of peak at 12.7 minutes: an aromatic nitrogen containing compound

Conclusion

As seen in this oil sample, the method of element, functional group, and ion prescreening described here provides a powerful tool for unknown identification. It saves time by leading the analyst directly to compound

types of interest. It provides higher confidence in library search identifications. In those cases of compounds that are not in the libraries, it provides useful information that can be used to greatly expedite spectral interpretation.

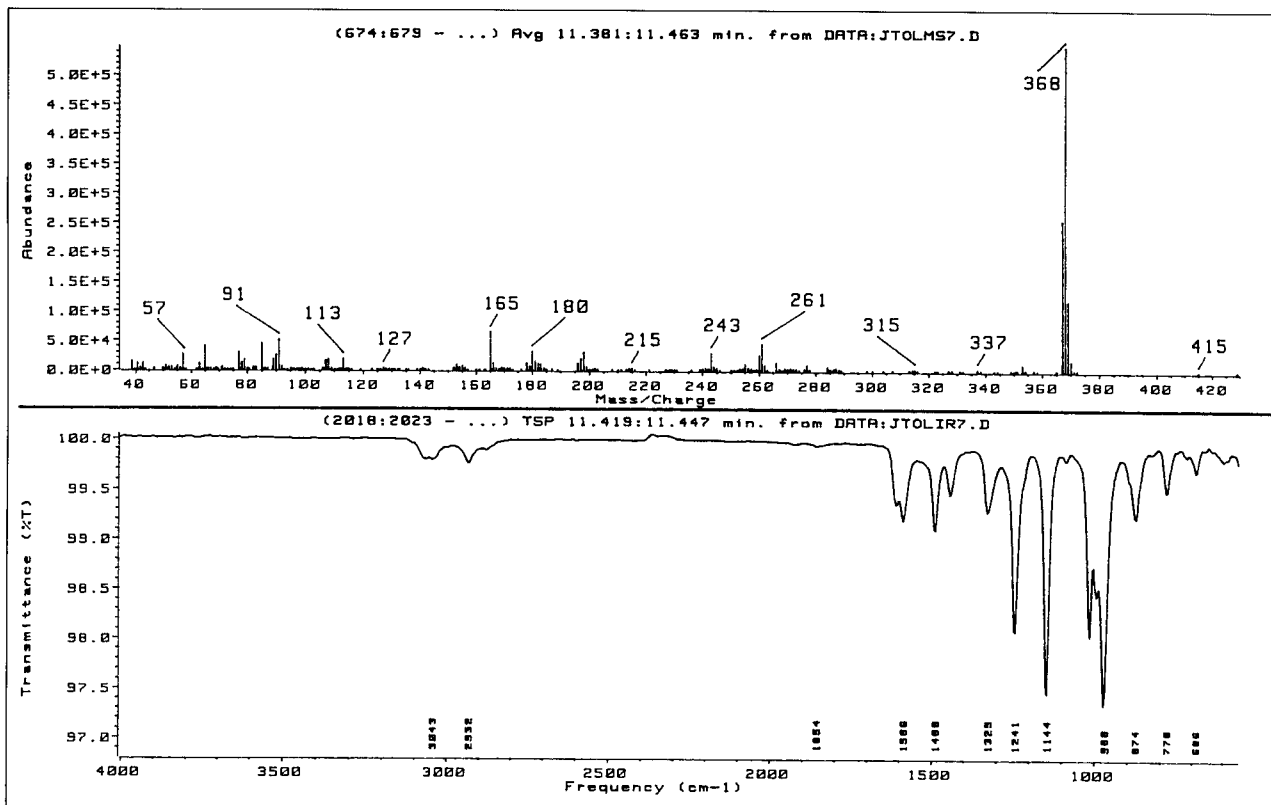


Figure 7. Infrared and mass spectra of peak at 11.4 minutes: trimeta cresyl phosphate

References

1. Leibrand, R. J. and Duncan, W. P., *Investigation of the Chromatographic Optimization of Combined GC/FTIR/MS*, Int. Lab., 1989, 46-52.
2. Leibrand, R. J., *Operation of Combined GC/IRD/MSD*, Hewlett-Packard Operating Note, 05965-90028.
3. Quimby, B. D. and Sullivan, J. J., *Evaluation of a Microwave Cavity, Discharge Tube, and Gas Flow System for Combined Gas Chromatography-Atomic Emission Detection*, Anal. Chem., 1990, 1027-1034.
4. Sullivan, J. J. and Quimby, B. D., *Characterization of a Computerized Photodiode Array Spectrometer for Gas Chromatography-Atomic Emission Spectrometry*, Anal. Chem., 1990, 1034-1043.
5. Duncan, W. P. and Nehr Korn, D., *Analysis of Hydraulic Oil Additives by GC/IR/MS*, Hewlett Packard Applications Brief, 23-5954-8207

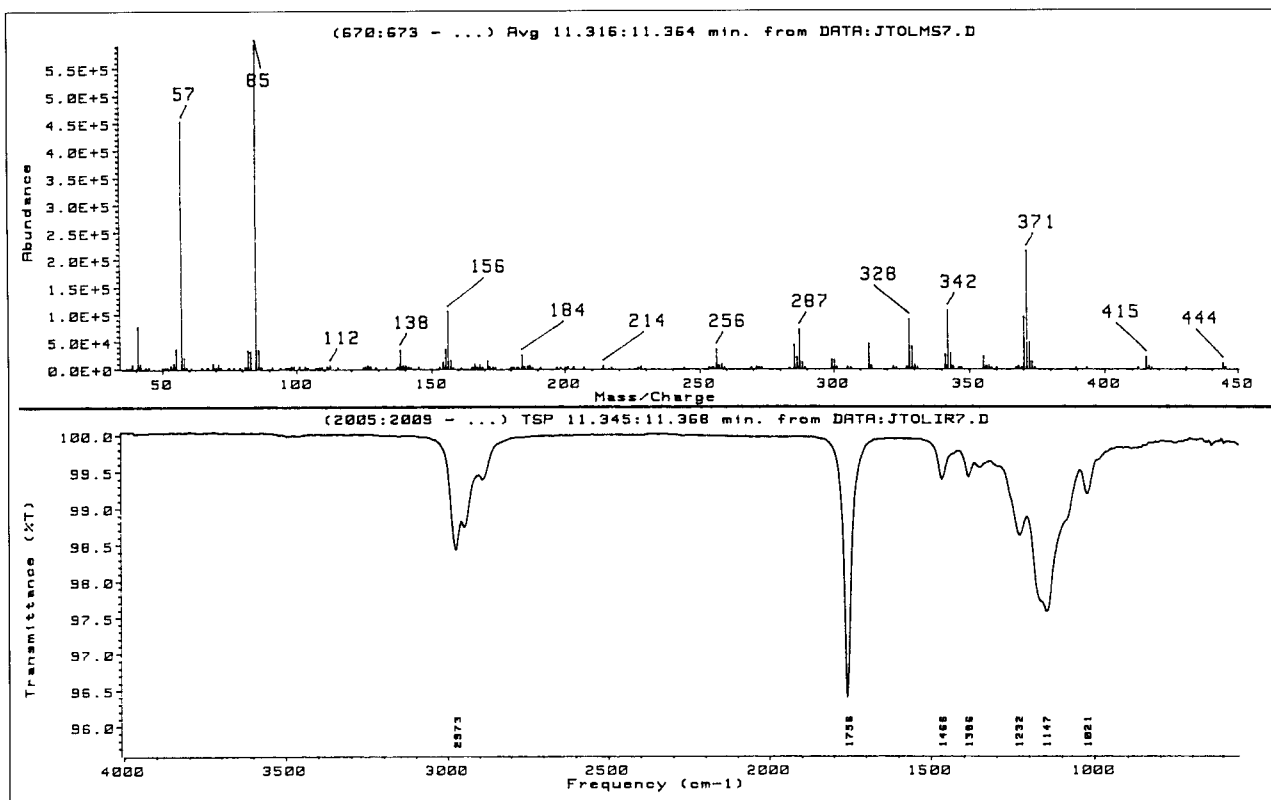


Figure 8. Infrared and mass spectra of peak at 11.3 minutes: a long chain diester

Conditions

Gas chromatograph

(for IRD/MSD system)

Column: 16 m × 0.32 mm id × 0.52 micrometer film of HP-1 (methyl silicone)

Carrier Gas: Helium at 40kPa, 2.0 mL/min constant flow

Oven: 80°C to 300°C at 20°C/min with 10 min hold

Injection Port: 300°C

Sample Injection: 0.4 microliters, splitless, 10% in iso-octane

IRD parameters

Light Pipe: 300°C

Transfer Lines: 300°C

Sweep Gas: Nitrogen, 35 kPa inlet, 100kPa outlet

Scan Parameters: 8 cm⁻¹ resolution, 2 coads, 3 scans/second stored

Detector: Wide Band MCT, 550 to 4000 cm⁻¹

MSD parameters

Mass Range: 35 to 400 daltons, 3 to 10 minutes; 35 to 600 daltons, 10 to 22 minutes

Scan Parameters: 2 A/D samples, 1.4 scans/second stored, 3 to 10 minutes; 1.0 scans/second stored, 10 to 22 minutes

Gas chromatograph

(for AED system)

Column: 15m × 0.53 mm × 0.15 micrometer film of DB-1 (methyl silicone)

Carrier Gas: Helium at 7 mL/min constant flow

Oven: 60°C to 320°C at 20°C/min with 10 min hold

Injection Port: cool on column, oven track mode

Sample Injection: 1.0 µL, 2% in iso-octane

AED parameters

Cavity: 350°C

Transfer Line: 320°C

COMPARISON OF RESULTS FROM

PBM Search of Library file: DATA:WILEY.L
 Avg 11.316:11.364 min. from DATA:JTOLMS7.D

AND

IR Search of Library file: DATA:REF.L
 ASP 11.345:11.368 min. from DATA:JTOLIR7.D
 JET ENGINE OIL

 Class 1 (on both lists)

**** NO COMMON COMPOUNDS FOUND IN SEPARATE REPORTS ****

 Class 2 (in only one library)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
1.	057866-21-4	12	---	371	C20H21NO6	2,3-Dimethylcolchicine
2.		---	941	182	C10H14O3	FURFURYL 2-METHYLBUTYRATE
3.	024817-51-4	---	939	206	C13H18O2	PHENETHYL 2-METHYLBUTYRATE, 95+%
4.	010032-15-2	---	939	186	C11H22O2	HEXYL 2-METHYLBUTANOATE, 98+%, F
5.		---	938	142	C8H14O2	2-PROPEN-1-YL 2-METHYLBUTYRATE
6.		---	937	192	C12H16O2	BENZYL 2-METHYLBUTYRATE
7.	000122-43-0	---	936	192	C12H16O2	ACETIC ACID, PHENYL-, BUTYL ESTE

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

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
8.	000141-04-8	---	961	258	C14H26O4	ADIPIC ACID, DIISOBUTYL ESTER
9.	000133-08-4	---	948	216	C11H20O4	DIETHYL BUTYLMALONATE, 99%
10.	001190-39-2	---	947	216	C11H20O4	MALONIC ACID, DIBUTYL ESTER
11.	007779-81-9	---	943	156	C9H16O2	ISOBUTYL ANGELATE, 98+%

Figure 9. Combined library search results for peak at 11.3 minutes