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Acquisition and analysis of combined GC/MSD and GC/FID data

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GC/MSD and GC/FID

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Application Note

Abstract

Combined GC/MSD and GC/FID data acquisition and analysis are demonstrated. Useful instrument configurations are described for single and dual column analyses. The ability to identify and quantify compounds based on the dual detector data is demonstrated.

Instruments

Agilent Technologies 6890 with other Hewlett-Packard instruments and data systems were used.

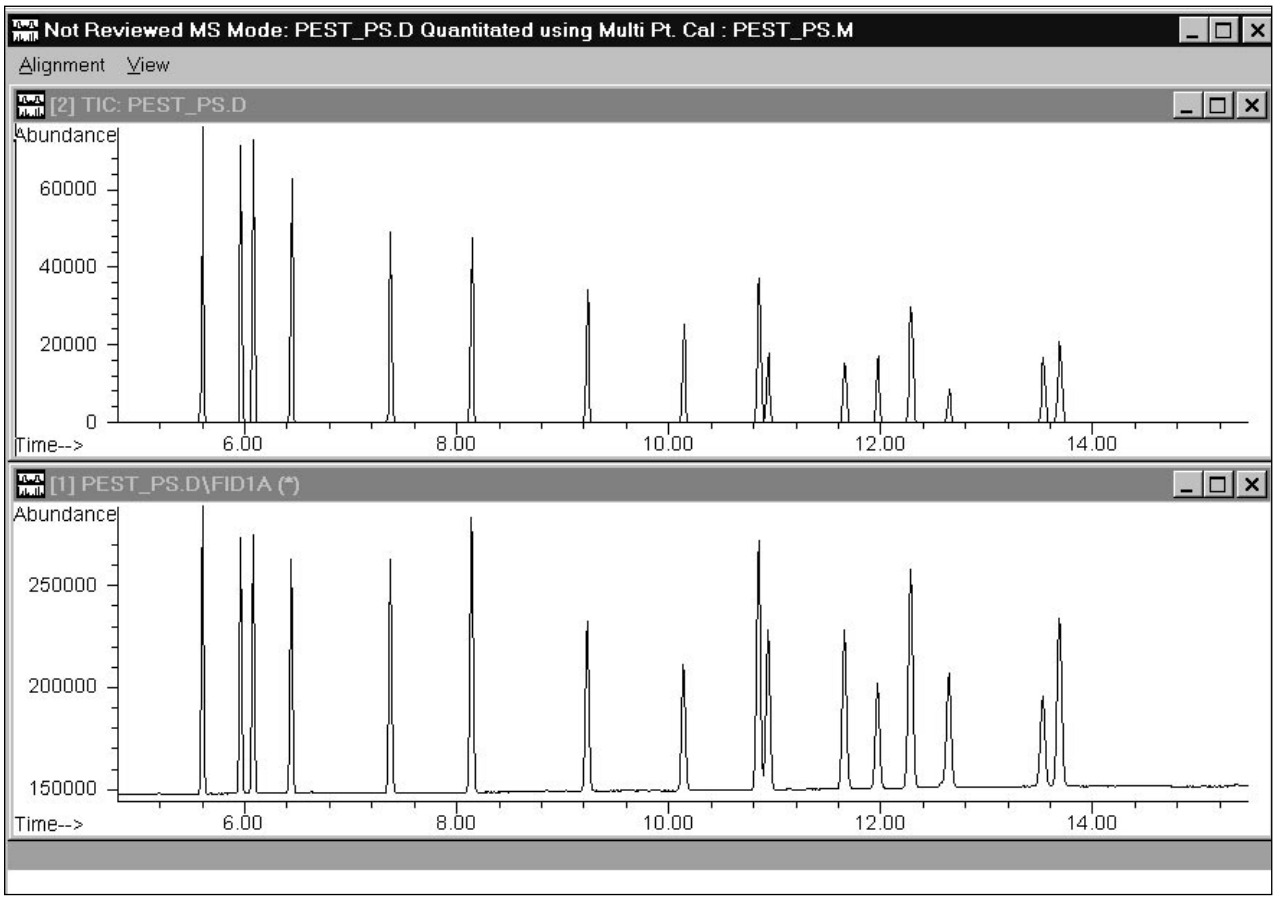

Figure 1. Single Column Pesticide Standard Aligned.

Introduction

There is growing interest in combining GC detectors with MSD to increase the information available from analyses. The combined data has several benefits:

- Identification with mass spectra
- Quantitation by GC detector
- Faster method development
- Maximum information from each analysis

This type of analysis has application in chemical reaction intermediate studies, industrial hygiene at waste or spill sites, and environmental analysis. Combined data can be used in several ways, such as:

1. Quantitation by non-selective GC detector (FID/TCD) with identification by mass spectra.
2. Additional confirmation with mass spectra as well as a selective GC detector such Nitrogen Phosphorus, Electron Capture, or Flame Photometric detector
3. A combination of the first two by using MSD and two GC detectors.

The performance of gas chromatography with simultaneous detection by MSD and GC detectors provides several technical challenges. The sample has to be resolved into its components chromatographically and then delivered to the two or more detectors (MSD and GC). Combined data can be acquired by using two columns with two detectors or a single column with a post column split to go to the two detectors. In this note, only the case of the MSD plus one GC detector will be discussed. Even this case offers at least three different injection port, column, and detector configurations.

Although it was possible in the past to simultaneously collect GC and MSD data, the MSD ChemStation did not provide tools for comparison or quantitation of mixed data signals. The recently introduced MSD Productivity ChemStation (revision A.03.00, available since August 1996) has added several tools in data analysis for display, comparison, and quantitation of the combined data.

Single Column Configuration

This is the recommended configuration. Only a single injection port and injector are required and the separations are accomplished on a single column. The sample is introduced onto a single column and then split post-column to the two detectors. Constant flow control in the column is very important so that the post column split between the detectors remains constant. The simplest single column configuration is to connect the column outlet to two transfer lines using a press-fit glass “Y” connector. This type of connector is readily available and has proven to be quite reliable with standard fused silica capillary columns.

Dual Column Configuration

In this configuration two matched (in length, diameter and phase) columns are used; one of the columns is connected directly to the MSD and the other to the GC detector. Both columns can be connected to a single inlet using a two-holed ferrule. The advantages are a single injector, a single injection port, and a single injection of the sample. The disadvantage of a single column head pressure is that the flow to the MSD will always be faster due to the vacuum. This will result in differing retention behavior on the two columns. One possible solution would be to use a lower restriction column to the GC detector to exactly match the flows. Another dual column configuration is to install the columns into two separate inlets. This allows matching retention times by controlling the head pressure for each column. The biggest disadvantage of this configuration is having to simultaneously inject into two injection ports for each sample. For any two column configuration, having exactly matched columns is important.

Signal Alignment

As was stated above, the differences between detectors (MSD vacuum versus atmospheric pressure GC detector) can cause a difference in retention times. A tool has been added to data analysis that allows the GC signal to be time aligned with the MS signal based on a two point linear fit. This allows easy visual confirmation of peaks by displaying the aligned signals. More importantly, the aligned signal can be used to set up a quantitation database (calibration) with GC signal quantitation and MS ion qualifiers for identification.

Experimental Conditions

Instruments

The experiments were performed using a 6890 Series GC and a 5972 MSD controlled by a Productivity ChemStation. The 6890 was equipped with a capillary split/splitless inlet, a single automatic liquid sampler tower, and a flame ionization detector. All operating parameters of the system were set directly from the ChemStation's Instrument Control screen. The operating system was MS Windows 95®. The Productivity ChemStation was configured for Enhanced Quantitation. This data analysis configuration allowed for the quantitation of combined GC and MSD data. Two samples were used: the MSD performance evaluation mix (Table 1) and a pesticide standard (Table 2). The MSD and FID conditions are listed in Table 3.

Table 1. MSD Performance Evaluation Sample

Component	Concentration
Dodecane	10 ng
Biphenyl	10 ng
4-Chlorobiphenyl	10 ng
Methyl Palmitate	10 ng

Table 2. Pesticide Standard Components

Component	Concentration
Aldrin	900 ng
alpha-BHC	900 ng
beta-BHC	900 ng
delta-BHC	900 ng
gamma-BHC	900 ng
p, p-DDD	900 ng
p, p-DDE	900 ng
p, p-DDT	900 ng
Dieldrin	900 ng
Endosulfan I	900 ng
Endosulfan II	900 ng
Endosulfan sulfate	900 ng
Endrin	900 ng
Endrin aldehyde	900 ng
Heptachlor	900 ng
Heptachlor epoxide	900 ng

In order to collect the MSD data, a full scan method was set up after performing a maximum sensitivity autotune. Setting GC signal one to the appropriate detector signal, in this case the front detector, allows the system to collect the FID signal. The MSD and FID signals are collected into a single data container. Since the MSD is not normally turned on until after the solvent peak has eluted, the GC signal was also set to only save data after the solvent peak eluted. This was only done to make comparison and scaling more convenient, but is not required.

For both dual and single column experiments 30 m × 0.25 mm ID HP-5MS fused silica columns coated with 0.25 µm of 5% phenyl methyl silicone (HP P/N 19091S-433) were used. The carrier gas was helium.

Single Column with Post Column Split

A single column was installed in the front split/splitless inlet. The effluent from the column was split between the MSD and FID using a tapered fit quartz Y-connector (P/N 5181-3397) attached to outlet of the column. A press-fit can be made by applying finger pressure to the column pressing it

Table 3. MSD and FID Conditions

MSD Parameters	Value	Notes
Column Interface Temperature	280°C	6890 Thermal Auxiliary Zone 2
Tune	Autotune	Maximum Sensitivity
Solvent Delay	2.5 min	
Mass Range	50–550 amu	Full Scan Mode
Threshold	150	
Sampling	2	
FID Parameters		
Temperature	250°C	
Hydrogen Flow	40 mL/min	
Air Flow	450 mL/min	
Nitrogen Makeup Flow	45 mL/min	Constant Column + Makeup
Save Data Start	3.00 min	see text
Data Rate	5.0 Hz	

into the connector that is being heated by a heat gun. Note: Carrier gas should be flowing through the column during this procedure to prevent damage to the stationary phase.

Deactivated polyimide coated fused silica tubing was used as transfer lines to the detectors. A 30 cm length of 0.1 mm ID was connected to one leg of the Y and then inserted into the heated capillary direct interface to the MSD. A one meter length of 0.53 mm ID tubing was connected to the other leg and then to the FID. Table 4 lists the column and inlet conditions. The column flow was set to 1.5 mL/min and the inlet was operated in constant flow mode. This results in a split between the MSD and the FID of 1:1.6. The split can be adjusted by using different lengths or diameters for the transfer lines. Using Constant Flow Mode ensures that the split between the detectors will hold nearly constant during the column oven program.

Both the evaluation mix and the pesticide standard were analyzed. For the evaluation mix 1 µL was injected using the pulsed splitless mode. For the pesticide calibration mix, 1 µL was injected in split mode with a split ratio 30:1.

Dual Column Conditions

Two columns were installed into the front split/splitless inlet with a two-holed ferrule (P/N 5062-3581). One of the columns was connected directly to the MSD through the direct capillary interface and the other directly to the FID. The column settings in Table 5 reflect the

Table 4. Column and Inlet Conditions for Single Column

Inlet and Column Conditions Single Column		
Parameter	**MSD Performance Evaluation Sample**	**Pesticide Standard**
Inlet Connection	Front Split/Splitless	Front Split/Splitless
Detector Connection	FID/MSD	FID/MSD
Outlet Pressure	Ambient	Ambient
Injection Mode	Pulsed Splitless	Split
Inlet Control Mode	Constant Flow	Constant Flow
Inlet Pressure	18.9 psi	19.5 psi
Pulse Pressure/Split Flow	25.0 psi	45.0 mL/min
Pulse Time/Split Ratio	0.5 min	30:1
Initial Column Flow	1.5 mL/min	1.5 mL/min
Average Velocity	36 cm/sec	37 cm/sec
Initial Temperature (Hold Time)	90°C (1 min)	100°C
Temperature Program Rate	15°C/min	25°C/min
Final Temperature (Hold Time)	255°C (2 min)	200°C
Second Program Rate	—	3°C/min
Second Final Temperature (Hold Time)	—	245°C (1 min)
Average Velocity	36 cm/sec	37 cm/sec

Table 5. Column and Inlet Condition for Dual Column

Inlet and Column Conditions Dual Column		
Parameter	**Column 1**	**Column 2**
Detector Connection	FID	MSD
Outlet Pressure	Ambient	Vacuum
Inlet Connection	Front Split/Splitless	Front Split/Splitless
Injection Mode	Split	Split
Inlet Control Mode	Constant Pressure	Constant Pressure
Inlet Pressure	14.0 psi	14.0 psi
Split Flow	24 mL/min	24 mL/min
Split Ratio	17:1	24:1
Initial Column Flow	1.4 mL/min	1.0 mL/min
Average Velocity	44 cm/sec	28 cm/sec
Initial Temperature	80°C	80°C
Temperature Program Rate	20°C/min	20°C/min
Final Temperature	280°C	280°C
Final Hold Time	2 min	2 min

actual instrument setup. The column head pressure was set to 14.0 psi resulting in an initial flow of 1.0 mL/min in the column connected to the FID. The MSD column flow was 1.4 mL/min. 5 µL of the MSD Evaluation sample was injected in split mode at 100:1 split ratio.

Results and Discussion

Single Column Configuration

Because of the different outlet pressures and flows to the MSD and the GC detector, the flow restriction of the two transfer lines must be carefully balanced. The 6890 GC has the ability to automatically maintain constant column flow throughout the oven temperature program thus maintaining a constant split between the two detectors. This is called "constant flow mode" and is recommended for this configuration. In this example the MSD transfer line passed through a 20 centimeter heated transfer zone while the line to the GC detector was at the column oven temperature. If constant flow was not used in oven temperature programmed run, the flow to the MSD would stay nearly constant while the column flow would change. This would change the split of the flow between the MSD and the GC detector. In the worst case, it could even result in no flow going to the GC detector part way through the program because the flow would preferentially go to the MSD.

The combination of the overall column flow and the relative restriction of the two transfer lines must be carefully calculated to set up the desired split of sample between the two detectors. Since the transfer lines potentially have different hold up times there is again a potential offset in retention times between the two detectors. In this case, though, it will be a nearly constant offset throughout the chromatogram. In our example there was a small constant offset for all the peaks that the alignment tool easily compensated as shown. In Figure 1, the pesticide sample analyzed on the single column is displayed after alignment. Since only the relatively constant offset due to the different holdup times in the transfer lines is adjusted, the peak alignment is excellent across all 16 pesticide peaks. The maximum deviation is 0.01 min.

Dual Column Configuration.

The chromatogram for the evaluation sample injected into the dual column setup is shown in Figure 2. There is a substantial offset in the retention times due to the 40% difference in column flows. In Figure 3 the GC signal has been aligned to the MSD total ion chromatogram. This was done using the Align GC function. This is done by selecting **View/Align GC** in the data analysis menu bar. In this view, four chromatogram windows are displayed to pick the four alignment peaks; first MSD peak, first GC peak, last MSD peak, and last GC peak. The alignment peaks are picked simply by pressing the left mouse button and dragging a zoom box around the correct peak. The apex time of the chosen peak is determined by the ChemStation integrator. After selecting the alignment points, select **Alignment/Perform Alignment** in the Align GC menu bar. The signal will be displayed with the GC times adjusted by a linear fit. Select **View/Return to DA** and you will be prompted to save the alignment points. The alignment can then be applied to any data files analyzed using the method by selecting **Quantitate/Use Method Aligned GC** Trace and saving the method (this is convenient for sequences of data files). The alignment does not change the actual data files but rather the display of the data and quantitation report.

Examining Figure 3 carefully, you will notice that the two middle peaks of the GC signal do not line up exactly with the corresponding peaks of the MSD ion chromatogram. This is a consequence of the different flows in the two columns combined with a column oven temperature program. The peaks are actually eluting at different temperatures on the two columns and therefore do not perfectly align with the linear adjustment.

Reporting and Quantitation

The aligned signals can be used to set-up the quantitation database with the GC signal as the quant signal and up to three MS qualifier ions for each compound. The **Calibrate/Setup Quantitation** mode allows this to be accomplished graphically. First double click the right mouse button with the cursor on the GC peak to be added. The corresponding MS spectrum will appear below the GC chromatogram. Now add qualifiers by clicking both mouse buttons simultaneously with the cursor on the desired ion. This can also be done in the **Calibrate/Edit Compounds** panel by editing the **"Signals to be used for quantitation"** section.

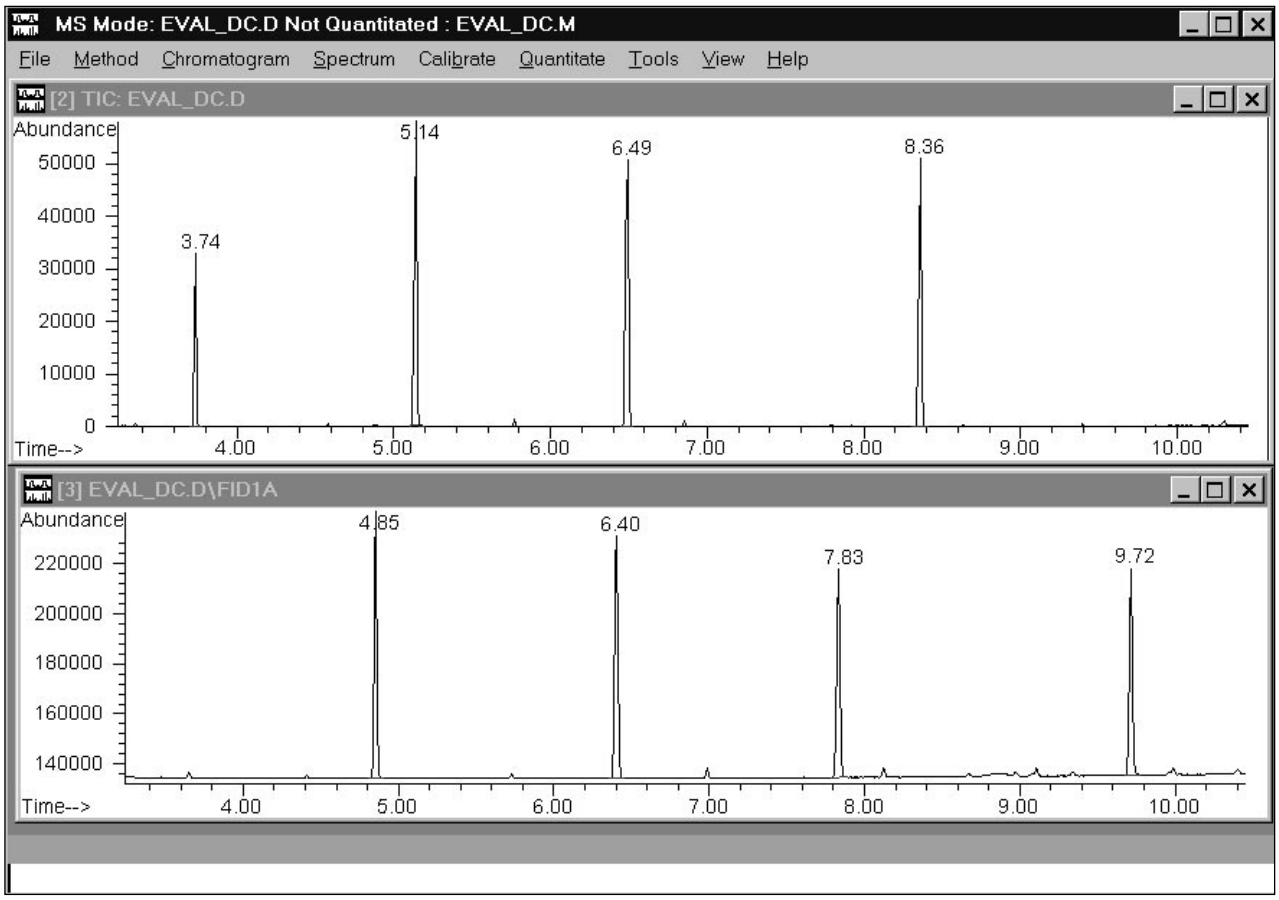

Figure 2. Dual Column Evaluation Sample Unaligned.

The detailed report style (selected in the **Quant Report Options** from **Edit Method** or **Generate Report**) can be used to see the complete details of the quantitation and identification. The report (Figure 4) is a "brief" report of mixed mode quantitation that was created using the Custom Reports feature of data analysis. All of the mixed mode report information is available to Custom Reports for increased reporting flexibility.

In order to verify quantitation by GC signal, performance calculations may be necessary. Calculation of performance parameters such as minimum detection limits or detector sensitivity require knowledge of the reporting units for the signals. The 5890, 6890, and the 35900 A/D modules produce differently scaled signals that also depend on the data handling system. The Table 6 lists the detector display units, area units, height units, and least significant values (LSVs) for the 5890 and 6890 GCs using the HP-IB data path of the Productivity ChemStation. Also included are units for the 35900 A/D expressed in terms of input signal to the A/D module. The height units correspond to the abundance units in the plotted chromatograms for GC Signals. Discussions of performance calculations and signal path units for the 5890 and 6890 GC are available in Technical Notes 1, 2.

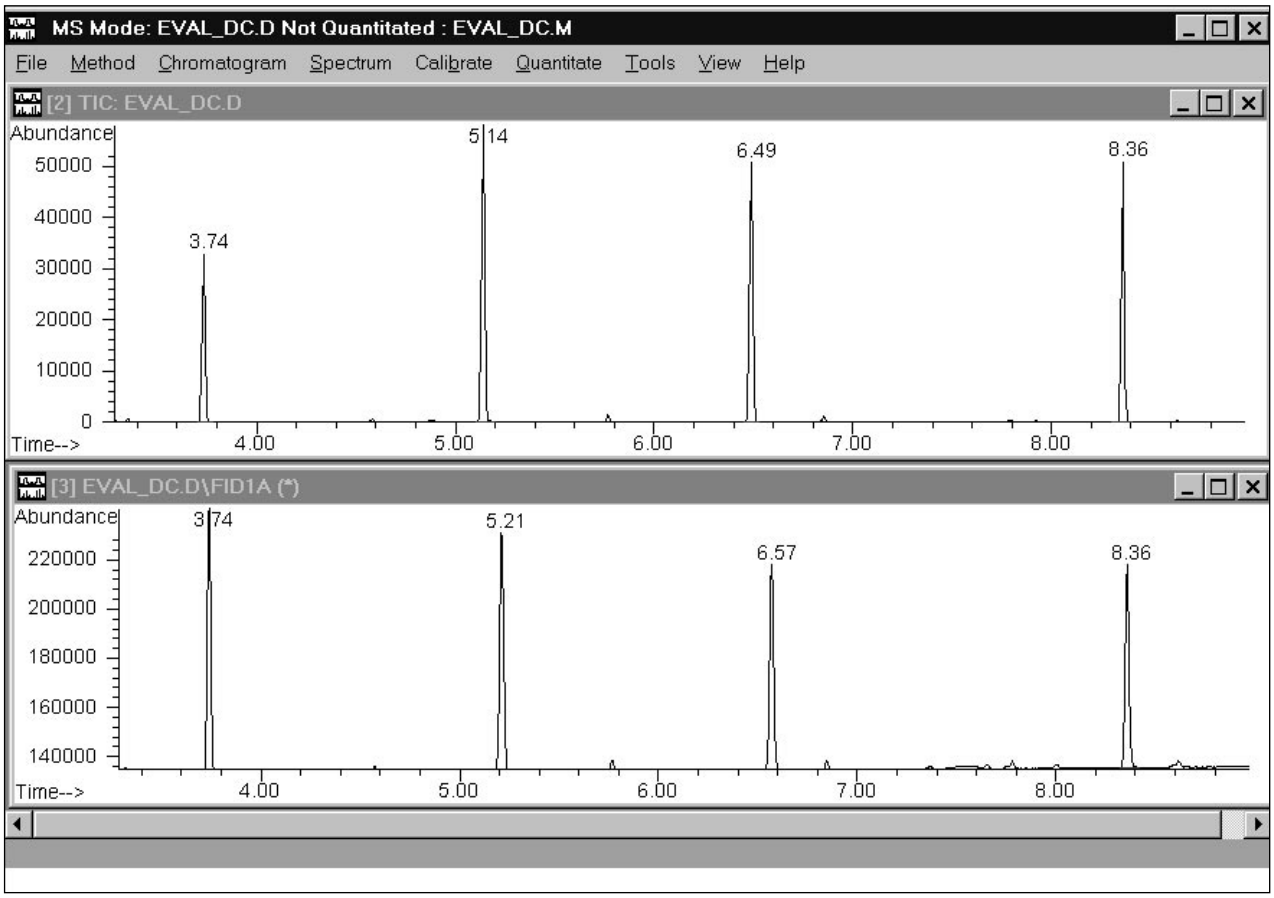

Figure 3. Dual Column Evaluation Sample Aligned.

Mixed Mode Data; GC Signal with MS Qualifiers

Data File Name: EVAL_PS.D
Operator: tjs
Data Acquired: 05/24/96 14:02

		Quantitation			Qualifier	
Name	**R.T.**	**ng**	**Signal**	**Area**	**Mass**	**Area**	**Ratio**
dodecane	4.62	6.5	GC1	10034532	57	542561	5.41
biphenyl	6.38	6.5	GC1	10796724	154	913483	8.46
4-Cl-biphenyl	8.03	6.3	GC1	8787460	188	686246	7.81
Me-palmitate	10.36	6.2	GC1	7222930	74	504034	6.98

Figure 4. Custom Report of Mixed Mode GC Quantitation with MS Qualifiers.

Table 6. Instrument Reporting Units and LSVs on the Productivity ChemStation

Instrument	Detector	Display Unit "a"	Area Unit "b"	Height Unit "b"	LSV "c"
6890	FID/NPD	1 pA	1.30×10^{-5} pA-sec	1.30×10^{-4} pA	1.30×10^{-4} pA
6890	TCD	25 µV	3.25×10^{-4} µV-sec	3.25×10^{-3} µV	3.25×10^{-3} µV
6890	ECD	5 Hz	6.51×10^{-5} Hz-sec	6.51×10^{-4} Hz	6.51×10^{-4} Hz
6890	AIB **d**	15 µV **e**	1.95×10^{-4} µV-sec **e**	1.95×10^{-3} µV **e**	1.95×10^{-3} µV **e**
5890	FID/NPD	1 pA	5.1×10^{-4} pA-sec	5.1×10^{-3} pA	5.1×10^{-3} pA
5890	TCD	25 µV	0.0127 µV-sec	0.127 µV	0.127 µV
5890	ECD	10 Hz	5.1×10^{-3} Hz-sec	0.051 Hz	0.051 Hz
5890	AIB **d**	15 µV **e**	7.6×10^{-3} µV-sec **e**	0.076 µV **e**	0.076 µV **e**
35900	Any 0 –1V	N/A	1×10^{-3} µV-sec **e**	1×10^{-2} µV **e**	1×10^{-2} µV **e**

a Value of one count on front panel display of GC
b Value of one reported count on the ChemStation
c Least significant value of the data path that corresponds to one bit of data
d Analog input board (input other detector signals)
e Approximate values due to gain variation in analog circuitry
f Configurable by user in ChemStation method for acquisition.

Conclusions

The MSD Productivity ChemStation can be used to analyze samples with combined MSD and GC signals. A thorough understanding of the physical setup and chromatographic conditions is crucial to achieving satisfactory results. Experiments with dual and single columns showed that separation and identification will be easiest using a single column system. However, the column flow and transfer line restrictions must be set up properly to obtain a consistent split between the two detectors. An inlet system that can control the capillary column in constant flow mode is optimal for the single column setup.

Data analysis can display and quantify combined signals. The Align GC function allows for easy identification of peaks as well as quantitation. The mixed quantitation is available with standard reports as well as the custom reports.

Appendix A. Example Files of Mixed Data

The mixed data files created for this note are installed with the Productivity ChemStation. They are located in the directory **\hpchem\msdemo\mixed** as follows:

Name	Description
eval_dc.d	Evaluation sample dual column data file
eval_dc.m	Evaluation sample dual column method file
eval_ps.d	Evaluation sample single column data file
eval_ps.m	Evaluation sample single column method file includes example of mixed mode quantitation database used for example report in results section
pest_ps.d	Pesticide standard single column data file
pest_ps.m	Pesticide standard single column method file

References

1. Technical Note (23) 5965-1640E, "HP ChemStation for Gas Chromatography: Reporting Units, Significant Digits, and Threshold Values for HP 5890, HP 6890 and HP 35900 Data," July 1996.

2. Technical Note (23) 5964-0282E, "Calculation of Performance Factors for the HP 6890 Gas Chromatograph Using Different Data Handling Devices," August 1996.

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