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Enhancing Pesticide Analysis with a Highly Sensitive GC/MSD System

Application Note

Agilent Technologies 6890/5973 GC/MSD System

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Abstract

The 6890/5973 GC/MSD was used to determine repeatability and detection limits for pesticides. Electron Ionization (EI) was used to analyze the samples. Both selected ion monitoring (SIM) and scan data were collected. The 6890/5973 system was optimized to get the highest sensitivity possible. The repeatability-derived detection limit in SIM mode well exceeds 10-picogram (on-column) detectability for a group of fifteen pesticides. A G1701AA MS Productivity ChemStation controlled the instrumentation and was used for all data processing.

Keywords

GC/MSD, pesticides, detection limits

Introduction

The analysis of pesticides in water, foods, and soil is important worldwide. In the United States consumer awareness has led to significant changes in regulations. Concern for the environment and public health has spawned more stringent analytical testing requirements. Europe has been experiencing a similar trend. In the Asia-Pacific region, environmental issues have been gaining interest rapidly. Japan, in particular, has passed numerous clean air and water regulations over the last few years. In addition, the more expansive trade agreements with the US have forced governments in Latin America—particularly Mexico—to pay much closer attention to environmental testing.

Lower pesticide detection limits are one result of the growing interest in environmental monitoring. For example, European regulations demand no more than 0.1 µg/L total pesticides in drinking water—a level that is challenging to measure. Even though the use of gas chromatography/mass spectrometry (GC/MS) improves the identification of compounds, most GC/MS systems to date have been unable to reach the required low detection limits since this corresponds to detectability of mid-picogram quantities (assuming standard sample preparation protocols and 1-µL volume injections of final extracts). That is why laboratories have relied on the more sensitive technique of GC coupled with an electron capture detector (GC/ECD) for measuring pesticides. Now, however, with the advent of the 6890/5973 GC/MSD, environmental testing laboratories have an alternative. Compared to GC/ECD systems, the 6890/5973 GC/MSD is highly stable and just as sensitive while providing analyte specificity with the mass spectral information.

Optimized Instrumentation Meets Stringent Requirements

Recognizing the environmental testing market's need to have a highly sensitive, selective, and rugged benchtop MSD (mass selective detector), Agilent Technologies designed the 6890/5973 GC/MSD system to be capable of measuring analytes below the regulated limits. In electron ionization (EI) selected-ion

monitoring (SIM) mode, the GC/MSD delivers femtogram-level sensitivity. In EI scan mode, the system provides picogram-level sensitivity. The scan sensitivity specification for the GC/MSD is set with 1 picogram of octafluoronaphthalene, the lowest specification in the industry.

Specific design enhancements improve overall system performance. For the GC, a pulsed splitless injection transfers all of the sample to the column. The programmable temperature vaporization (PTV) inlet increases injection volume sizes from 1–5 µL up to 250 µL. With respect to mass selective detection, the 5973 MSD has a high energy dynode (HED) detector, independently heated ion source and quadrupole regions, and a faster data acquisition rate. The MS Productivity ChemStation not only supports the advances in the GC and MSD instruments but also provides tools for more flexible and productive data analysis for laboratories doing target compound analysis.

6890 GC

The newly designed split/splitless inlet of the 6890 GC is forward-pressure regulated during splitless operation, ensuring that all the sample reaches the column. The pulsed splitless mode also allows the user to inject up to 5 µL without losing any sample. This approach delivers five times greater sensitivity than could be achieved with the previous generation GC/MSD.

The PTV with the ALS is capable of delivering up 250 µL per analysis. For conventional sample preparation this increases sensitivity by 50 times over the maximum 5-µL injections into a splitless inlet. Alternatively, 10–50 times less sample is required for sample preparation if larger injections are made. Thus, a typical 1 L sample size could be reduced to 100 mL. Reducing the sample size reduces the laboratory waste and the expense of waste removal.

5973 MSD

With conventional detectors, the conversion of the high mass ions to electrons is less efficient for the slower moving, higher mass ions. The high energy dynode (HED) detector in the MSD improves sensitivity by increasing the efficiency of ion detection, particularly improving the detection of ions with m/z > 200.

Independently heated ion source and quadrupole zones give users the ability to select temperatures that preserve the integrity of the chromatographic separation, especially important for higher boiling point compounds. As a result, tailing is reduced significantly and there are no compromises between column temperature limits and ion source temperatures. (With previous MSD designs, the source temperature was determined by the conductance of heat from the interface. Source temperatures above 200°C were not easily attained. The interface temperature had an upper temperature limit based on the column installed. For example, the upper limit of an HP-5 MS column is 325°C so holding the interface at 325°C might provide a source temperature of 200–210°C; however, the chemical background from the column would be high.)

The scan data acquisition rate has been doubled compared to that of the 5972 MSD. It is quite common to have ten scans across a peak from a 250 µm ID column. The higher sampling rate gives excellent repeatability for extracted ion area counts. This also allows the use of 100 µm ID columns in scan mode. With 100 µm columns run times can be reduced by a factor of 5 while preserving the chromatographic separation.[1, 2]

MS Productivity ChemStation

Finally, tools previously released only with Agilent Technologies EnviroQuant environmental software are now available to any laboratory doing target compound analysis. EasyID is a tool for updating the retention times in

Results

Lowered Detection Limits

Figure 1 is a 1-µL pulsed splitless injection of the mixture of all fifteen pesticides with scan mode detection. The chromatogram represents 25 pg of each pesticide on column for fourteen of the fifteen pesticides. The fifteenth pesticide, coumaphos, did not respond well because it is such a high boiler. In subsequent work, it was found that increasing the source temperature improves the response of coumaphos relative to the increasing chromatographic baseline at the higher temperatures. (Note that higher source temperatures are also important for the analysis of PAHs, such as benzo(g,h,i)perylene.) Even with the lower source temperature, coumaphos is easily detected and quantitated in SIM mode as shown in Figure 2.

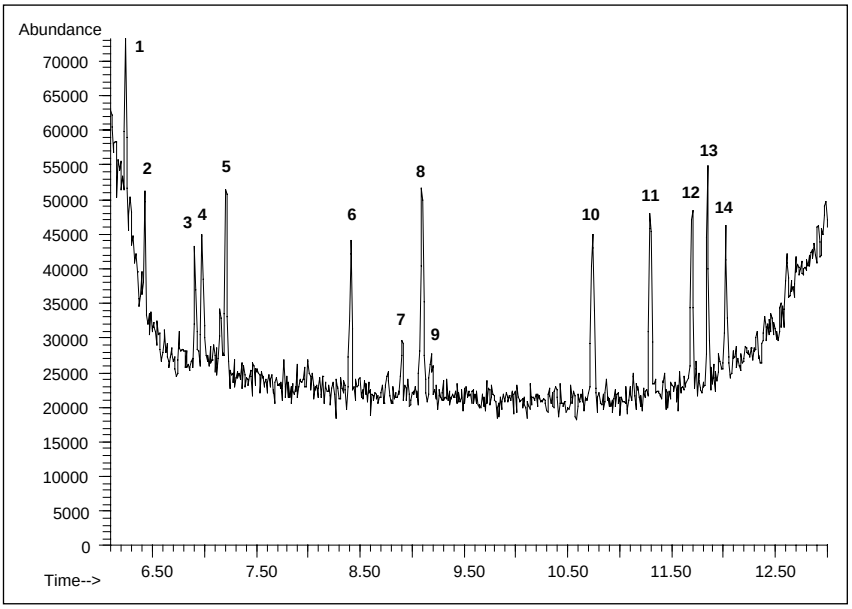

Figure 1. A Total Ion Chromatogram of the pesticide mix produced in scan mode for 25 pg each pesticide on-column. Fourteen of the fifteen pesticides are displayed. Coumaphos, #15, was lost in the TIC due to column bleed at the high temperature at which it elutes. Its response was also lower because of the low ion source temperature. It could be quantitated at this level under these operating conditions with its extracted ion. Moreover, with higher source temperatures, the response of coumaphos is comparable to those of other pesticides.

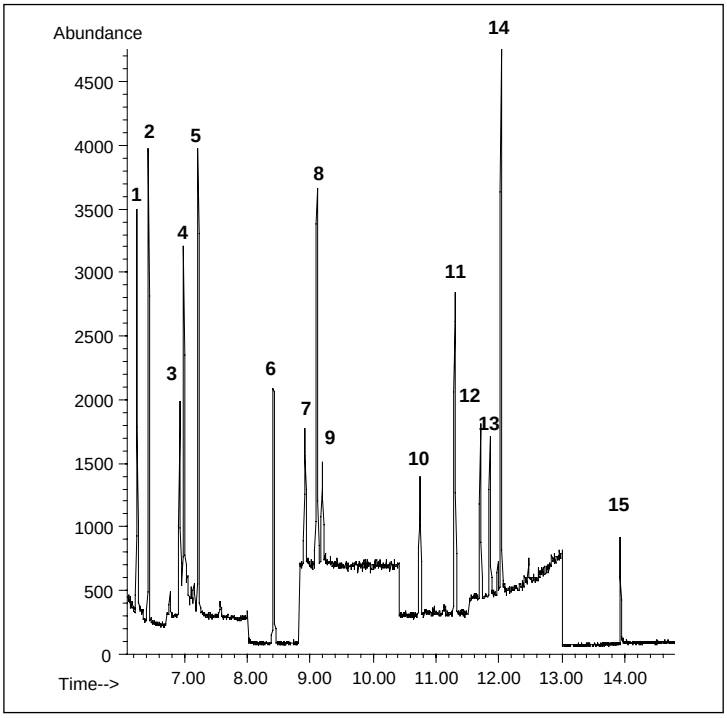

Figure 2. Total Ion Chromatogram of the pesticide mix produced by SIM of 10 pg each pesticide on-column. The changes in the baseline are due to ion group changes with time. Using multiple ion groups with fewer ions per group improves the sensitivity of the detector.

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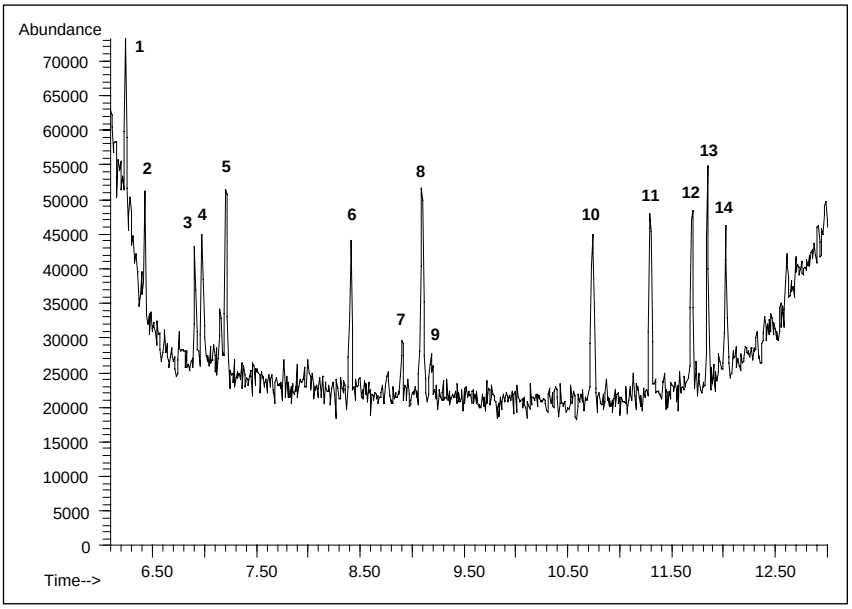

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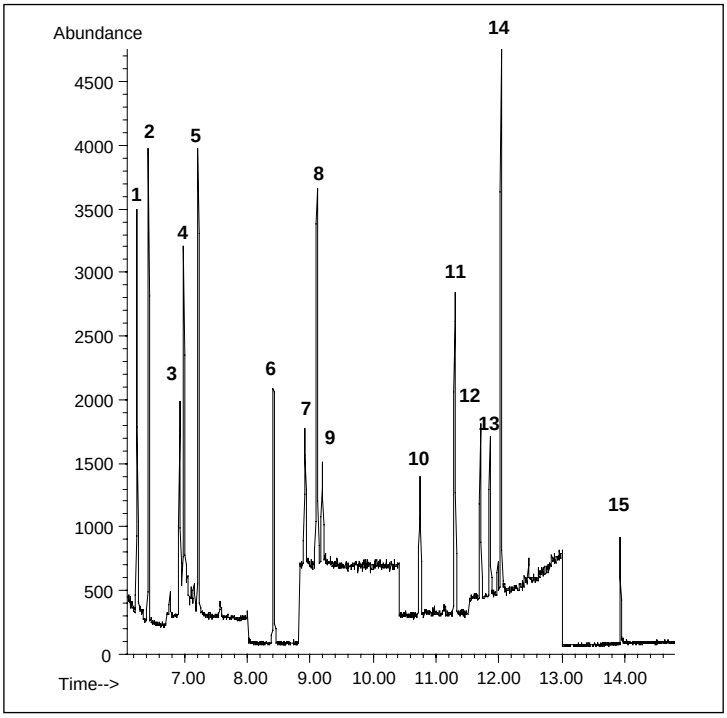

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Figure 2 is a SIM chromatogram for the fifteen pesticides listed in Table 2. It can be seen from the signal that the detection limit is well below 10 pg on-column (1 µL injection, 0.01 ng/µL each component).

The MSD's HED detector is a 10 kV high energy dynode, positioned 90° off-axis and shielded to minimize noise. The HED detector improves sensitivity by increasing the efficiency of ion detection. For example, Figure 3 is a spectrum of the pesticide endrin showing the enhanced high mass response of the HED detector. The ion at m/z = 263 is greatly enhanced over m/z = 81.

Using the m/z = 263 ion for quantitation improves detection limits for endrin. Because most pesticides have a strong fragmentation ion in the 200 amu range, the HED detector enhances the response of many pesticides. Moreover, using higher masses for quantitation improves detection limits for a second reason: higher masses have less system noise associated with them. Choosing the quantitation ion may not always be an option when running regulated methods. Check with the local regulating agency to confirm that an alternative quantitation ion can be used before employing performance based method changes.

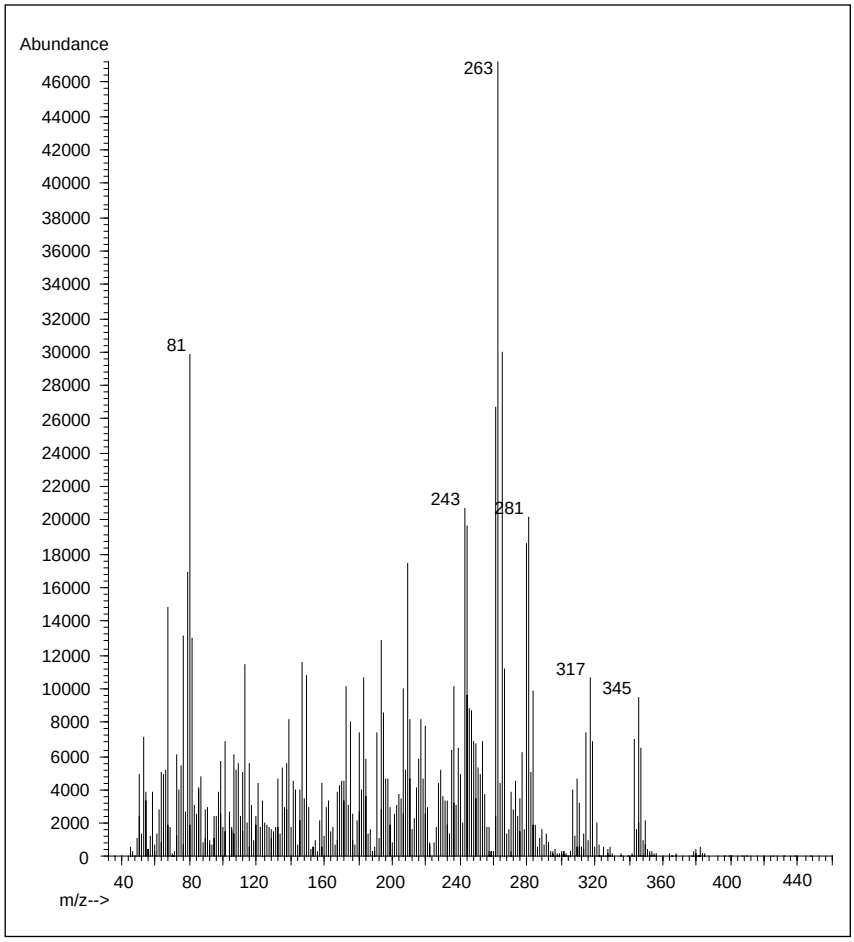

Figure 3. A spectrum for the pesticide endrin. The enhanced response of m/z = 263 relative to m/z = 81 is from the HED detector.

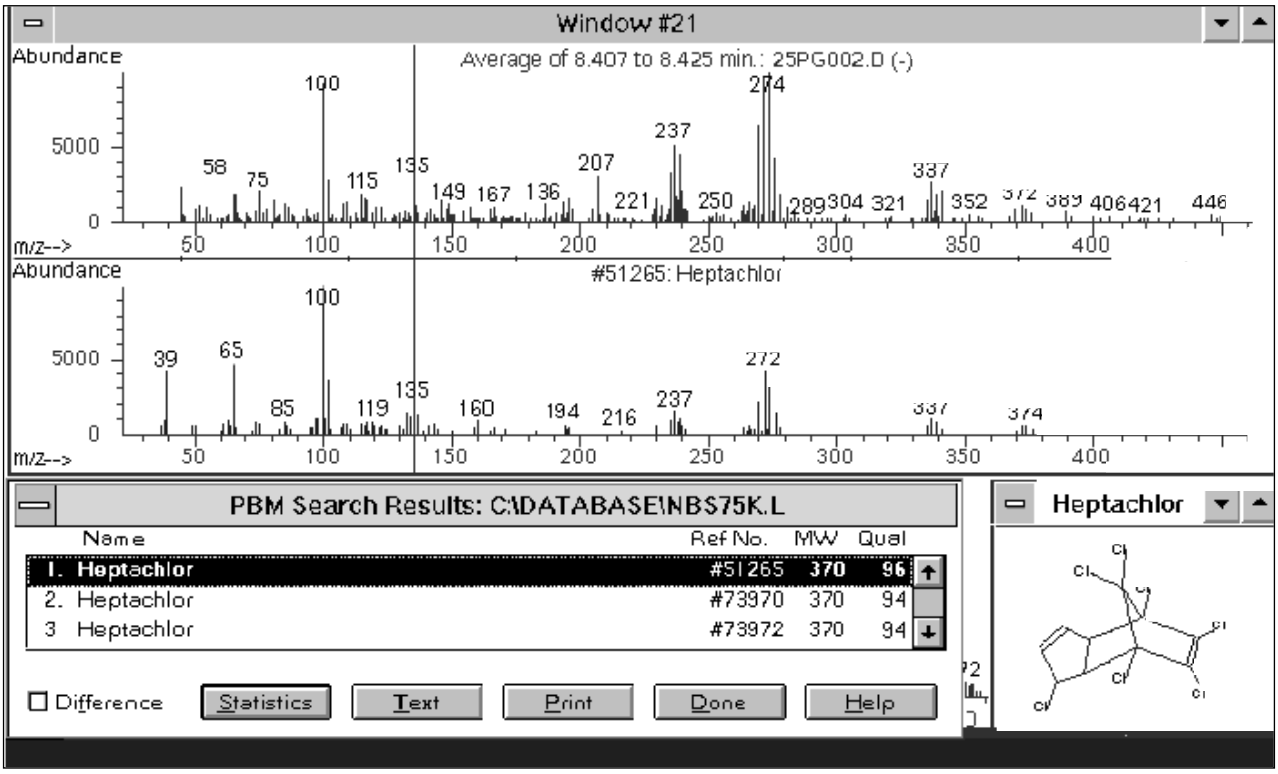

Figure 4. The high quality result of a search of library spectra identifying heptachlor, another example showing improved high mass response of the HED. The top spectrum is from 25 pg on-column. The bottom spectrum is the library match.

Figure 4 is a library search result for heptachlor at the 0.025 ng/µL concentration level. Even at low concentrations, 25 pg on-column, the library search result is 96. The enhanced high mass response of the HED detector helps to improve the library search results and quality. Since the search algorithm places more importance on higher mass ions, their strong presence ensures a better match quality.

Repeatability

Repeatability experiments were conducted at three concentrations for the fifteen pesticides using both the SIM and scan modes. Seven injections per concentration were used to calculate percent relative standard deviations (RSDs) for each compound. An overall percent RSD for each concentration was obtained by averaging the fifteen individual RSDs (Table 3). The detection limit was defined as the concentration at which repetitive injections gave RSDs for the extracted ion of no greater than 20%. As can be seen from the results in Table 3, the detection limit in scan is close to 0.01 ng injected onto the column. In SIM, the detection limit is well below the 0.01 ng level (Figure 2).

As a point of comparison to the limits of detection prior to the 5973 MSD, in scan mode, the previous generation (6890/5972 GC/MSD) had difficulty achieving the detection of pesticides at 0.01 (ppm) ng/µL level (1 µL injected).

Table 3. Overall Repeatability in Scan and SIM for the Fifteen Pesticides*

MS Mode	Concentration (ng/µL)	Average % RSD
Scan	1.00	2.61
	0.10	6.12
	0.01	19.45
SIM	1.00	1.84
	0.10	1.72
	0.01	3.78

* N = 7 injections, 1 µL injection volumes

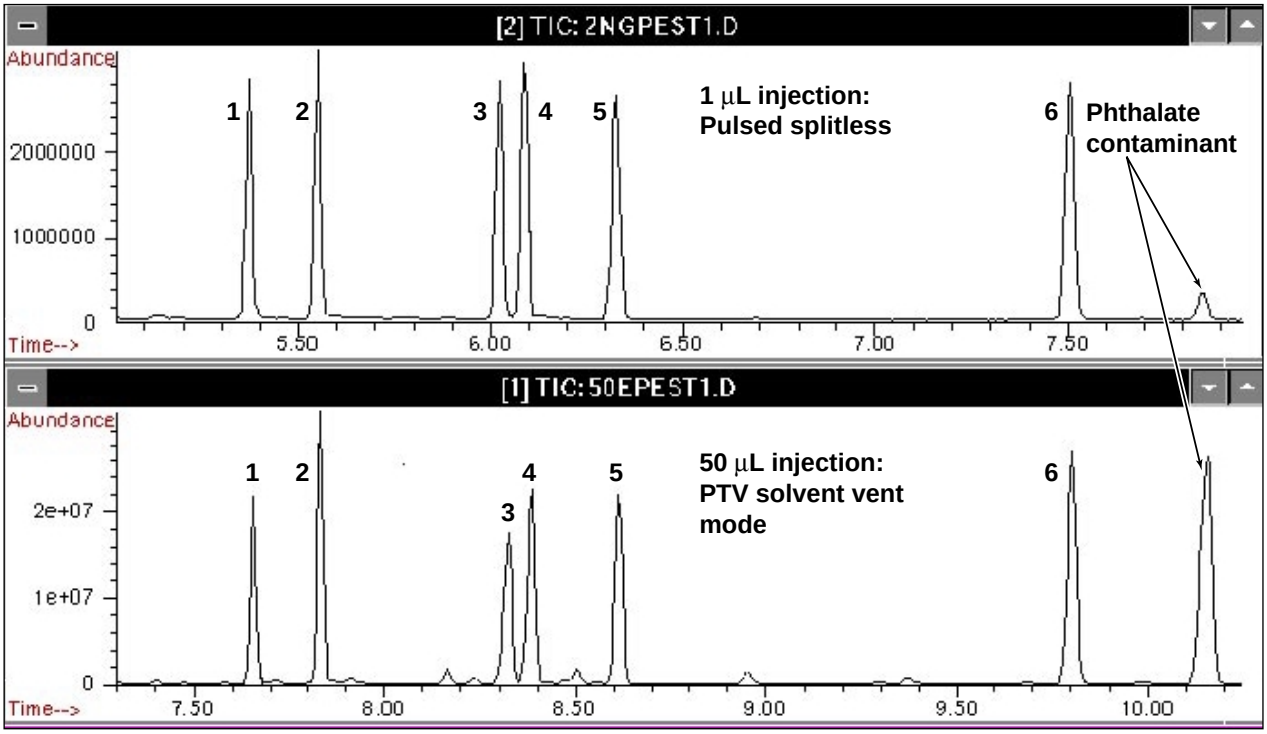

Figure 5. Chromatograms showing the performance of the PTV inlet compared to the conventional pulsed splitless inlet. The top chromatogram is a 1 µL injection of a 2 ng/µL pesticide mix. The bottom chromatogram is 50 µL (2 × 25 µL) of a 0.25 pg/µL mix. Notice that the chromatographic peak shape is not compromised with the large volume injection. Also notice that more phthalate contaminant from the solvent is present due to the additional concentration step, illustrating that high solvent purity is critical. Finally, note that while the retention times are shifted due to the longer injection process (concentration followed by ballistic heating), the relative retention times are unchanged.

Further Enhancements of Sensitivity with GC Inlets

Along with the sensitivity enhancement of the MSD, the programmable temperature vaporization (PTV) inlet allows for large volume injections up to 250 µL. By injecting larger samples, lower concentration samples can be run successfully. The PTV inlet was used in the solvent vent mode which allows large volume injections (> 10 µL). In order to use the conventional ALS, multiple injections of 25 µL (1 × 25 µL), 50 µL (2 × 25 µL), and 100 µL (4 × 25 µL) were made with a 50 µL syringe. In this approach, injections are made in series and solvent is vented while the analytes are trapped in the inlet. After the last injection the inlet is heated ballistically and the analytes are transferred to the column. A tutorial on using PTV can be found in reference 5.

In Figure 5, large volume injection with the PTV inlet is compared to injection with a conventional split/splitless inlet. Note that the chromatographic peak shape is not compromised by injecting large amounts. This is because the solvent is vented and does not flood the column. It is important to remember not to exceed the capacity of the column. For example, a 30 m × 0.25 mm (250 µm) ID column with a 0.25 µm film has a upper capacity of ~ 80 ng/component.[6]

Another important factor when using large volume injections is solvent cleanliness. The bottom chromatogram—the same standard with the PTV in the solvent vent mode—illustrates that small contaminants with high boiling points can also be concentrated by the PTV inlet. (However, as both chromatograms in Figure 5 indicate, in this analysis, the solvent contaminants do not interfere with the analytes of interest.)

Conclusions

Pesticide repeatability data were used in the usual manner to determine detection limits for both SIM and scan modes. In SIM, the 6890/5973 GC/MSD system was able to measure analytes at much lower levels than with previous MSDs. The detection limits are now very well-matched to measurement ranges prescribed by European environmental regulations.

These test results demonstrate that the technological advancements inherent in the 6890/5973 MSD system have greatly improved the system's sensitivity. The 6890 GC makes it possible to get all of the injected sample to the MSD. By using pulsed splitless injection with a conventional split/splitless inlet, up to 5 µL of sample can be quantitatively transferred to the analytical GC column, enhancing the detectability of the system five fold. In addition, the introduction of the PTV inlet allows the transfer of up to 250 µL quantitatively.

The new HED detector provides five times more sensitivity than the previous GC/MSD. In addition, it runs at a lower multiplier voltage, which contributes to a longer multiplier lifetime. The independently heated ion source makes it possible to choose a temperature that preserves the integrity of the chromatographic separation, especially for higher boiling point compounds. The gold quadrupole has improved resolution and scan range (1.6–800 amu) and with its independent heating is able to stabilize faster and remain stable longer. Finally, the higher data acquisition rate improves chromatographic integrity and precision in area counts. For the same scan range and averaging, the points across a GC peak have doubled.

In all, results demonstrate that to be productive, especially when doing trace analysis, the 6890/5973 GC/MSD with the MSD Productivity ChemStation comprise the system of choice.

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