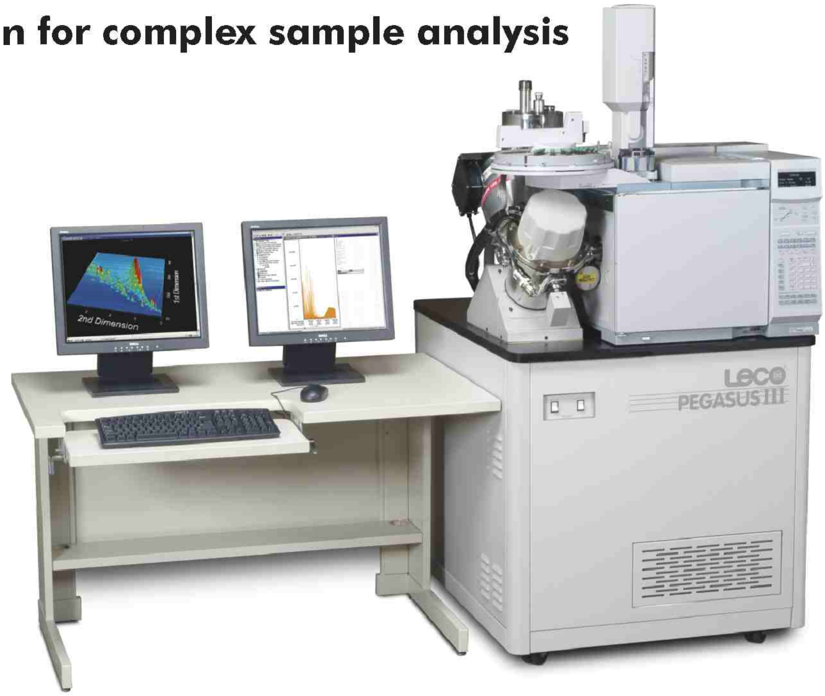
LECO®

PEGASUS® 4D GCxGC-TOFMS

Looking Beyond the Peaks… LECO's Pegasus 4D

Increased analytical resolution for complex sample analysis

GCxGC, combined with LECO's Pegasus® III GC-TOFMS, changes the perspective of complex sample analysis. No longer limited to two analytical dimensions, the ***Pegasus 4D GCxGC-TOFMS*** *system provides you with four dimensions of analytical resolution for significantly more complete complex sample analysis.*



The GCxGC Advantage

The demands of complex samples (such as the gasoline sample shown in Figure 1) quickly overwhelm traditional GC-MS analysis techniques. The wide range of analyte concentrations within the sample, combined with the high degree of analyte coelution, make accurate characterization of the mixture impossible. Consequently, important sample information is lost.

GCxGC adds a second dimension of chromatographic resolution to the sample analysis. This is accomplished using two distinct stationary phases (such as non-polar and polar) within a single analysis. The use of these two separation mechanisms expands the chromatographic plane—thus creating additional space in which peaks can be resolved.

The GCxGC analysis of the gasoline sample (shown in Figure 2) reveals the expanded chromatographic plane and improved analyte resolution. More analytes are detected in the sample and the reduction of chromatographic coelution yields more accurate analyte identifications. More information about the complex sample is gained without any appreciable increase in the separation time.

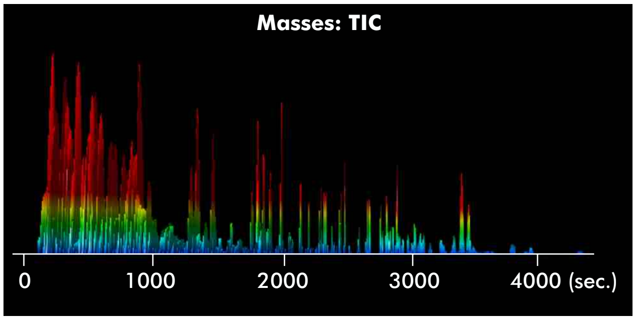


Figure 1: Traditional GC-MS Analysis of gasoline (678 analytes detected)

LECO's GCxGC Thermal Modulator is the key to the enhancement of chromatographic resolution obtained by our Pegasus 4D system. The modulator, placed between the non-polar and polar stationary phases, consists of a robust quad jet system that creates two distinct LN2-cooled trapping zones to ensure that all of the effluent from the first column is properly focused prior to thermal release to the second column. A secondary column oven is also provided for optimization of the second dimension separation.

The entire modulator is mounted inside an Agilent 6890N gas chromatograph. Control of the GC autosampler (Agilent 7683 or CTC CombiPAL), GC, LECO's GCxGC Thermal Modulator, and Pegasus III GC-TOFMS is fully integrated within a single computer using LECO's versatile **ChromaTOF® operating software**. Fully integrated GC-MS and GCxGC-MS instrument control, fully automated data processing, and a variety of paper and electronic reporting options are just a few of the features that set ChromaTOF apart.

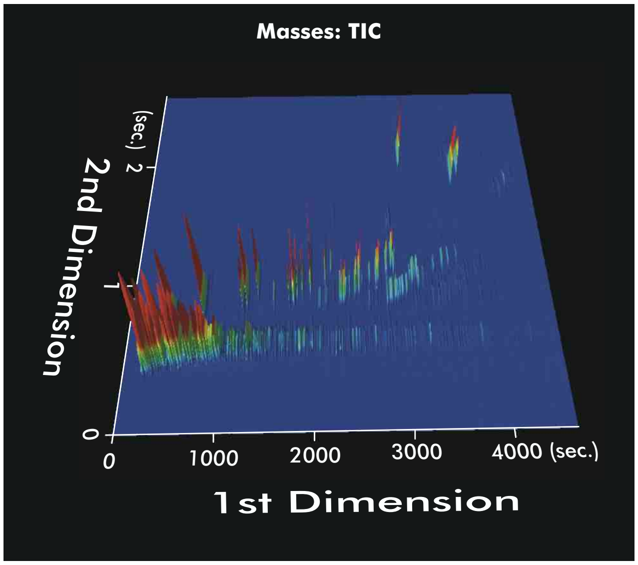


Figure 2: GCxGC-TOFMS Analysis of gasoline (1,246 analytes detected)

The Power of Time-of-Flight Mass Spectrometry

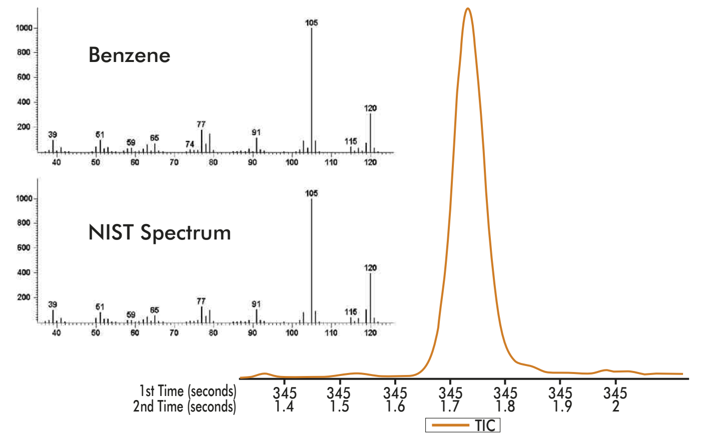


Figure 3: The 150-millisecond-wide trimethyl benzene GCxGC peak is easily defined and identified at a mass spectral acquisition rate of 150 spectra/second

As part of the focusing process in the GCxGC modulator, analyte bands that elute from the first column are significantly sharpened prior to being released to the second column. As a result, peaks ranging between 50- and 200-milliseconds wide (Figure 3) are produced. These narrow peak widths require a detection system that is capable of collecting data at rates of 100 Hz or more in order to adequately characterize the shape of the chromatographic peak.

Only LECO's Pegasus III TOFMS, with full mass range spectral acquisition rates up to 500 Hz offers MS data with sufficient density to address the unique requirements of GCxGC separations. Spectral quality at these higher acquisition rates is also maintained in the Pegasus III system, as seen in the trimethyl benzene spectrum (Figure 3).

The addition of TOFMS detection to the GCxGC system offers distinct qualitative analysis benefits. By nature of the orthogonal separation system used in GCxGC analyses, very structured chromatograms are produced showing distinct bands of analytes grouped by specific chemical characteristics (Figure 4). Using these chemical characteristics as a guide, more accurate individual analyte identification can be obtained from the TOFMS system.

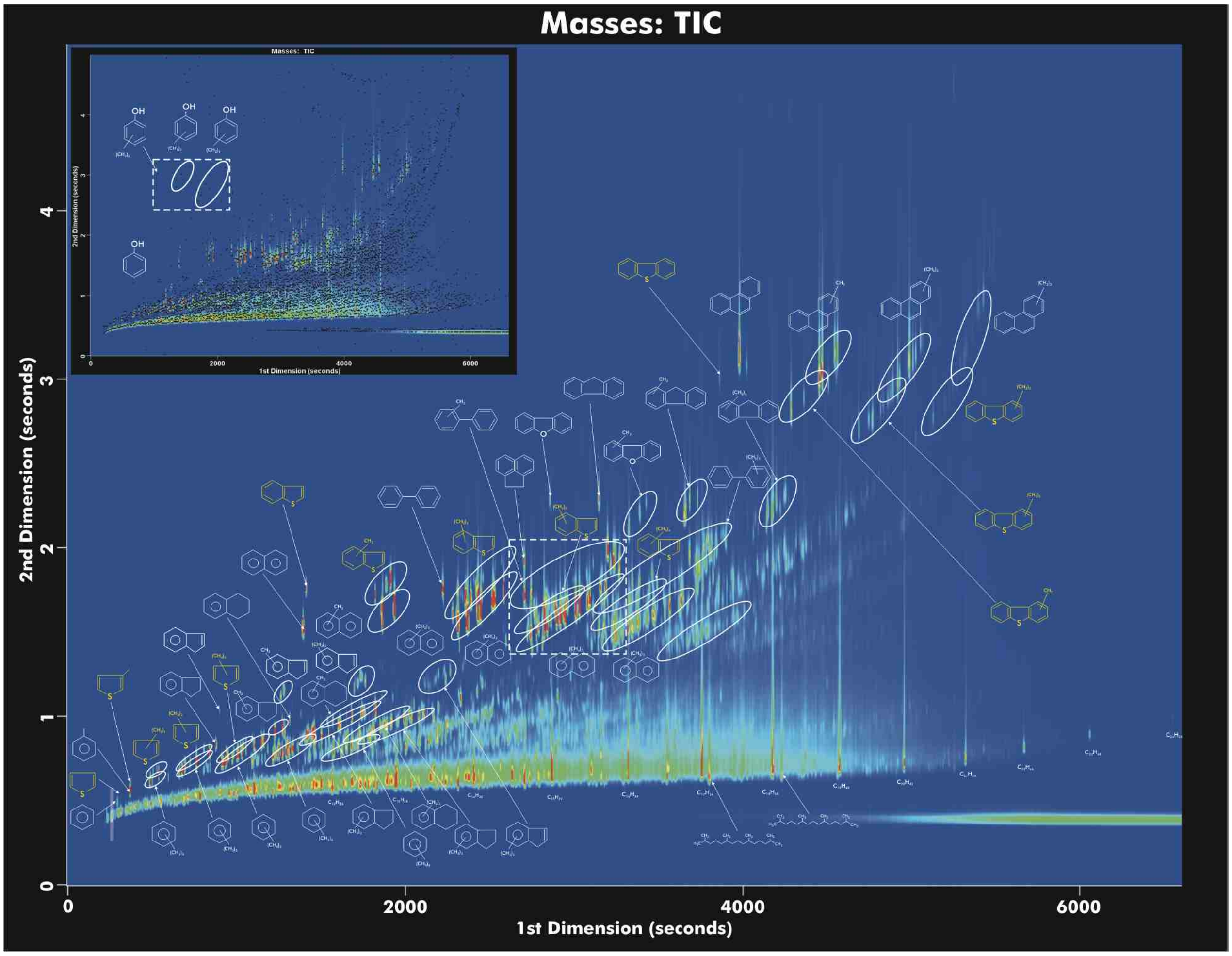


Figure 4: Complex sample characterization of diesel fuel is significantly simplified by the combination of the structured GCxGC chromatogram that produces distinct bands for analyte chemical classes, and Time-of-Flight mass spectrometry which provides specific analyte identifications

ChromaTOF—An Added Dimension of Analytical Resolution

In addition to offering fully integrated system control from a single computer and software package, LECO's ChromaTOF operating software provides fully automated processing of GCxGC-TOFMS data files. From easily prepared Data Processing Methods, a complete sample assay can be obtained—including comprehensive qualitative characterization of the sample and/or quantitative analysis of specific analytes in the mixture. Data reporting is also simplified with a variety of custom report and electronic data export capabilities that are available for automatic transmission at the end of the analysis.

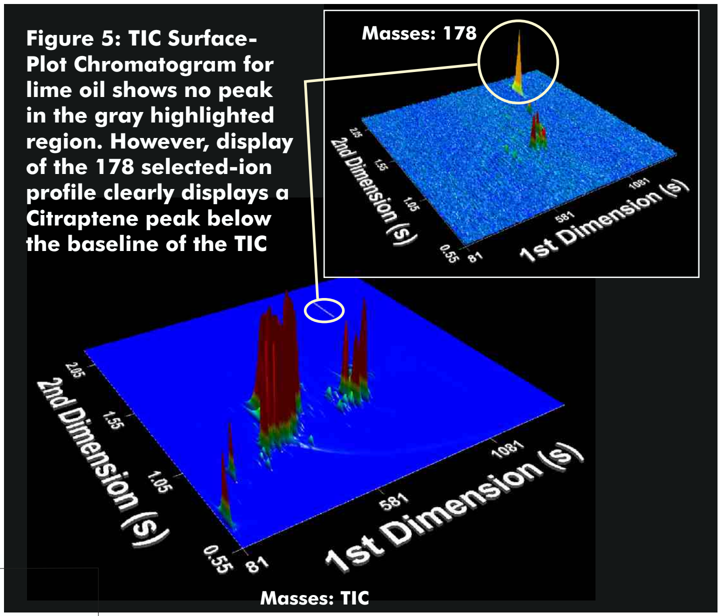


Figure 5: TIC Surface-Plot Chromatogram for lime oil shows no peak in the gray highlighted region. However, display of the 178 selected-ion profile clearly displays a Citraptene peak below the baseline of the TIC

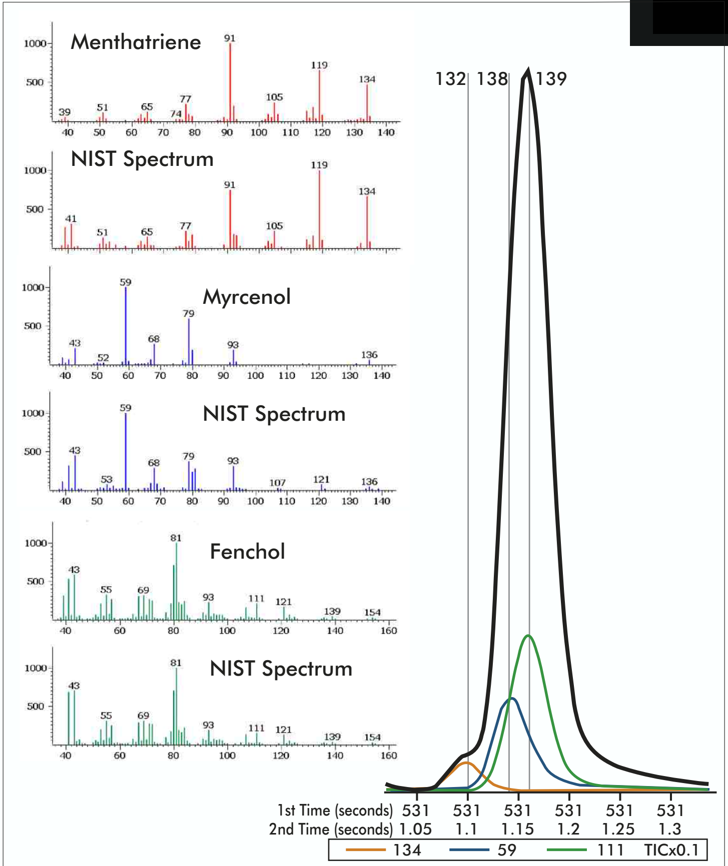


Figure 6: Automated Peak Find of three coeluting analytes in a 0.3-second portion of a second-dimension chromatogram that was obtained from the GCxGC-TOFMS analysis of lime oil. The Mass Spectral Deconvolution algorithm provides accurate full range mass spectra free of interferences from the coeluting analytes. Shared ion signal is accurately proportioned between the coeluting analytes for better spectral accuracy

Qualitative Sample Characterization

By providing the ChromaTOF software with only an expected peak width and a signal-to-noise threshold, automatic location of all peaks within the chromatogram is possible. Peaks included are those buried beneath the background of the reconstructed total ion current chromatogram (TIC) or those that coelute with other analytes in the sample. Figure 5 shows a TIC surface plot with a section of empty baseline highlighted toward the back of the chromatogram. Using the Peak Find algorithm, the ChromaTOF software locates a small analyte peak situated beneath the TIC baseline. The validity of this small peak is shown in the inset selected ion profile chromatogram.

Coelutions are also automatically detected using the Peak Find algorithm. Figure 6 shows a 0.3-second segment of a second-dimension chromatogram. The black line represents the scaled TIC, which reveals a small shoulder on an otherwise gaussian peak shape. The automated Peak Find algorithm actually locates three peaks in this region: one, creating the shoulder in the TIC; and a coelution of two other components beneath the gaussian portion of the TIC. Masses that are unique to these analytes are determined by the Peak Find algorithm and displayed for review.

Once a coelution is identified, ChromaTOF's unique Mass Spectral Deconvolution algorithm automatically extracts a clean mass spectrum for each detected analyte. The extracted mass spectra are free of interfering signal from sample background or other coeluting analytes. In Figure 6, the extracted mass spectra for the three coeluting analytes are displayed. The small Menthatriene spectrum (displayed as the orange peak in the chromatogram and orange mass spectrum) shows a good NIST library similarity of 860 (86%). The Myrcenol (blue peak) and exo-Fenchol (green peak) elute much more closely. These analytes also share quite a bit of common signal in the 79-81u, 93u, and 136u regions of their mass spectrum. The Mass Spectral Deconvolution algorithm is able to accurately proportion shared signal between the two coeluting analytes, resulting in accurate full-mass range identifications for Myrcenol (NIST similarity of 762) and exo-Fenchol (NIST similarity of 967).

Automated Quantitative GCxGC-TOFMS Analysis

ChromaTOF software also offers a fully automated quantitative analysis package for use with GCxGC-TOFMS data. A full range of options for analyte calibration (such as external calibration, an unlimited number of internal standards, an unlimited number of calibration points, multi-order calibration curves, individual point weighting factors, logarithmic calibration curves, and origin weighting) are available. A variety of report and electronic export options are also available for distribution of the quantified results.

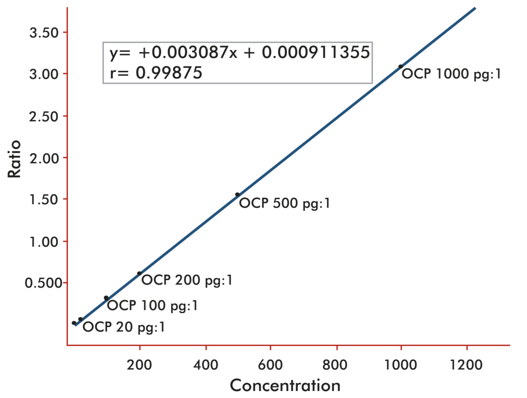


Figure 7: 4,4′-DDE calibration curve from 0.2 pg/µL to 1000 pg/µL

Analyte Calibration

Figure 7 depicts a GCxGC-TOFMS calibration curve for the organochlorine pesticide degradate 4,4′-DDE. The calibration ranges from 0.2 pg to 1000 pg on column to address the requirements for pesticide analyses in food matrices. The high- and low-level 246u extracted ion profiles are displayed, along with the mass spectrum for the 0.2 pg/µL and 1000 pg/µL standards in Figure 8. Good linearity is observed across the range, with a correlation coefficient of 0.999 obtained for the calibration curve.

Sample Quantification

Trace level quantification is frequently complicated by matrix interferences. In Figure 9, the matrix components of a cucumber extract are clearly displayed in the surface-plot TIC. The added resolving power of GCxGC successfully moves the 4,4′-DDE peak away from the congested matrix region for easier and more accurate quantification.

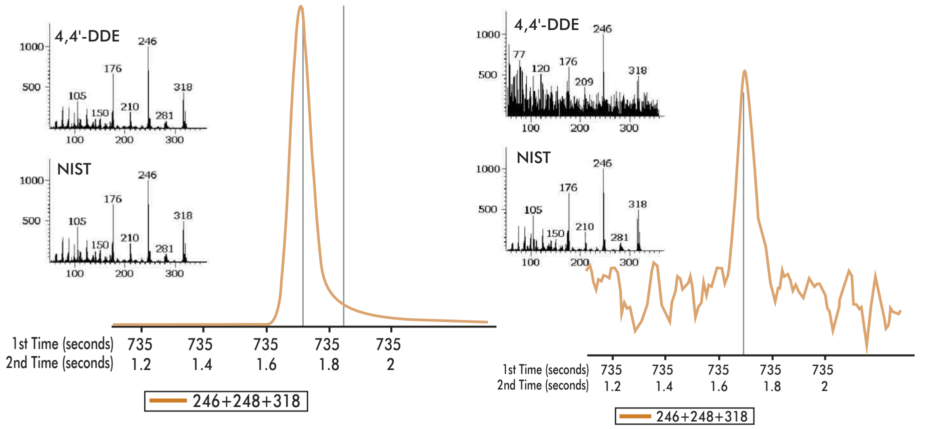


Figure 8: 1000 pg (left) and 0.2pg (right) 4,4′-DDE Standards

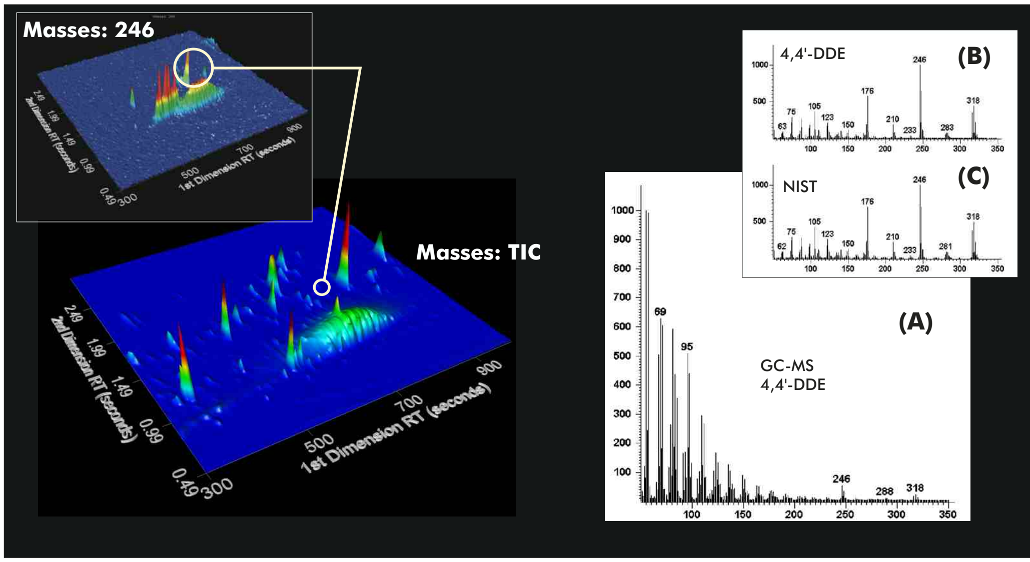
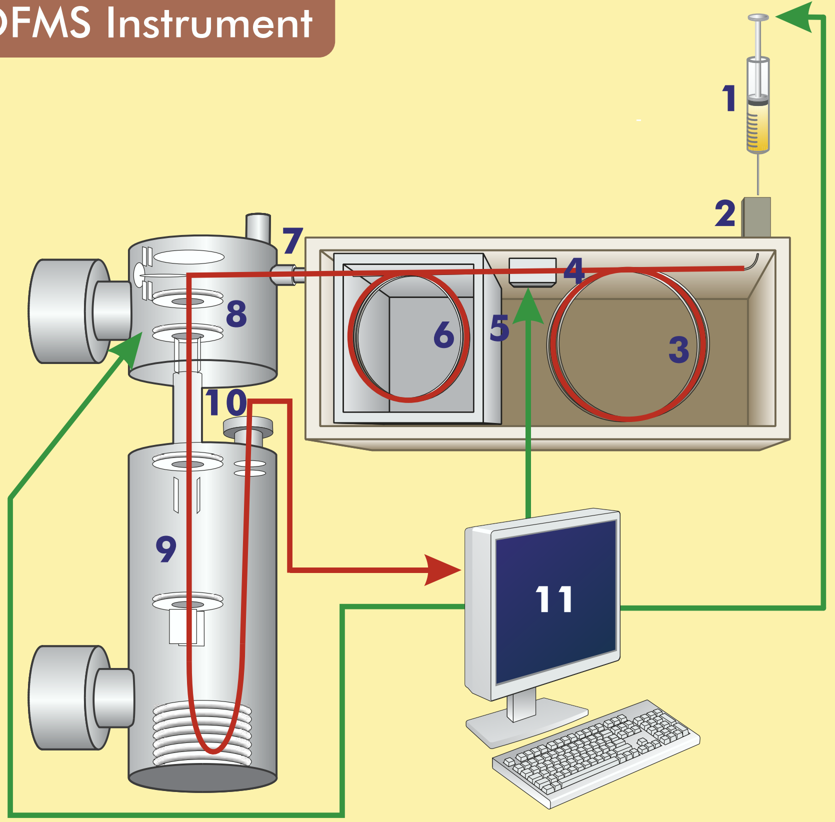


Figure 9: Analysis of 2 pg of 4,4′-DDE in a cucumber extract. No peak is observed in the surface plot TIC. Without GCxGC separation the 4,4′-DDE peak is difficult to identify among the cucumber matrix interferences (A). With GCxGC separation the 4,4′-DDE peak is easily identified (B) by an NIST library search (C)

Diagram of GCxGC-TOFMS Instrument

1. **Sample**
2. **Inlet**
3. **First-dimension column**
4. **Modulator**
5. **Secondary oven**
6. **Second-dimension column**
7. **Transfer line**
8. **Ion source**
9. **Flight tube**
10. **Time-array detector**
11. **Instrument control/data processing computer**



LECO—Advanced Separation Science for the Working World

Unique® LC-TOFMS

- Benchtop design makes the Unique the smallest LC-TOFMS on the market
- Multi-anode detection system improves dynamic range, provides mass accuracy independent of compound concentrations, and has low noise effects
- Gridless quadratic field in the linear mass analyzer provides improved ion transmission, which benefits sensitivity

GCxGC

- Offers enhanced separating power for complex sample analysis
- Easy-to-use software based on ChromaTOF®
- Classification software feature simplifies component identification
- Flame Ionization Detector (FID) and Electron Capture Detector (ECD) models available

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