An Executive Summary

Using Magnetic Sector GC-HRMS in a Commercial Dioxin Lab

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Introduction

Persistent organic pollutants (POPs) are toxic chemicals produced intentionally or as byproducts of industrial and agricultural activity. Due to their persistence, many of these compounds migrate naturally from the environment into plant food sources and up the food chain where they bioaccumulate in the fatty tissue of animals. Magnetic sector gas chromatography–high-resolution mass spectrometry (GC-HRMS) systems are the highest performing mass spectrometers available for the routine target compound analysis of dioxins and POPs in all kinds of sample matrices. The practical use of these instruments has come a long way since 2005, when attaching two gas chromatographs to one source was new for magnetic sector instruments. This technique now provides full compliance worldwide with any regulatory method for detecting dioxins, polychlorinated biphenyls (PCBs), or polybrominated diphenyl ethers (PBDEs) in food and environmental matrices. This webcast summary explains how magnetic sector GC-HRMS can be used in a commercial POPs laboratory to increase throughput for dioxin analysis and presents data for the analysis of PCBs, organochlorine pesticides (OCPs), and PBDEs. This piece also presents the results of experiments designed to test the suitability and capabilities of magnetic sector GC-HRMS for target compound analysis, including precision, accuracy, and identification capabilities in targeted workflows as well as the software's ease of use and effectiveness.

Dioxins and the Thermo Scientific DFS Magnetic Sector GC-HRMS

In the early 1980s, researchers found a buildup of dioxins in herring gull eggs, and the release of these chemicals was traced to pulp and paper mill manufacturers. In 1989, the US Environmental Protection Agency (EPA) issued one of the first dioxin methods, EPA 1613, which specified minimum levels of 10–100 pg/L or 1–10 ng/kg. To test these sample types, early dioxin analyses were run using a Finnigan 3200 GC-MS instrument. Detection limits were adequate for the time, but with only single-unit resolution, specificity was limited and rigorous cleanup was required. Therefore, the development of dioxin methods such as EPA 1613 led to the need for GC-HRMS systems. Such higher resolution (>10,000) instruments have sensitivities less than 1 pg injected (one part per quadrillion, 10-15) and create fewer false–positives, which is especially important for the most toxic dioxin chemicals such as tetrachlorodibenzo-p-dioxins (TCDDs).

More recently, the Stockholm Convention has been the driver for HRMS and especially for dioxin detection. The Convention was established in 2001 and includes 179 different countries

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or parties. Initially concerned with only 12 byproducts and manmade chemicals, several more compounds were added in 2009 under the Stockholm Convention.

To detect dioxin levels, one can use two GC instruments, as shown with the Thermo Scientific™ DFS™ Magnetic Sector GC-HRMS in the schematic in **Figure 1**. Using two GC systems does not double sample analysis throughput, but it certainly improves it because two different chemistries can be run off the same instrument. Analysts can use a dioxin column placed in one GC instrument, and a PCB column in the second instrument so that analysis can switch back and forth between two methods without venting the MS source.

HRMS Mainstream: PCB and PBDE

Although the production of PCBs is banned, there are still unintended sources. For example, yellow dyes contain PCB-11 and building materials like caulks also contain PCBs. EPA Method 1668 was first introduced in 1997 for 12 dioxin-like PCBs and six markers. It has been revised many times since then and has expanded to include 209 congeners of PCBs with 27 carbon-13 labeled standards, which significantly complicating the method. With the current EPA Method 1668, a five- or a six-point calibration is run for the 27 standards and a single-point calibration for the remainder of the compounds (182) is performed. Unfortunately, no single column can resolve all 209 compounds of interest and MS systems' dwell times on each one of the ions is short, which limits sensitivity. Thus, GC-HRMS system can provide the resolution that GC-MS instruments alone cannot.

Brominated diphenyl ethers have also been an issue in the last 15 to 18 years as a potential contamination source and their concentrations in the environment are of concern. For many of these compounds, HRMS instrumentation is not required, however HRMS systems can provide better sensitivity and isotope dilution can be used. Since brominated diphenyl ethers are increasingly prevalent in the environment, they can be found in food matrices that require detection in the low part per trillion range. When analyzing a matrix from a regulatory point of view, detection limits are important. When tracking compounds, it is more important to have an absolute value to determine if levels are increasing or decreasing, thus requiring the capabilities of HRMS systems.

Methods for Polycyclic Aromatic Hydrocarbons (PAHs), Tributyltin, N-nitrosodimethylamine (NDMA), Nonylphenyls, and Organochlorine Pesticides

Several additional methods can be run on a HRMS system. While HPLC instruments with UV and fluorescence detectors or GC/FID can be used for PAH analyses, US EPA methods now all require GC-MS. While GC-MS detection limits are adequate for regulatory purposes, they may not be low enough for the detailed investigation work that is suited for GC-HRMS analysis.

Figure 2 illustrates the analysis of fish samples exposed to a fire in a commercial freezer. The local authorities would not release fish store in adjacent freezers until they were certain no PAH present. A testing method capable of detecting PAH in fish tissue at 0.1–0.3 parts per billion was needed.

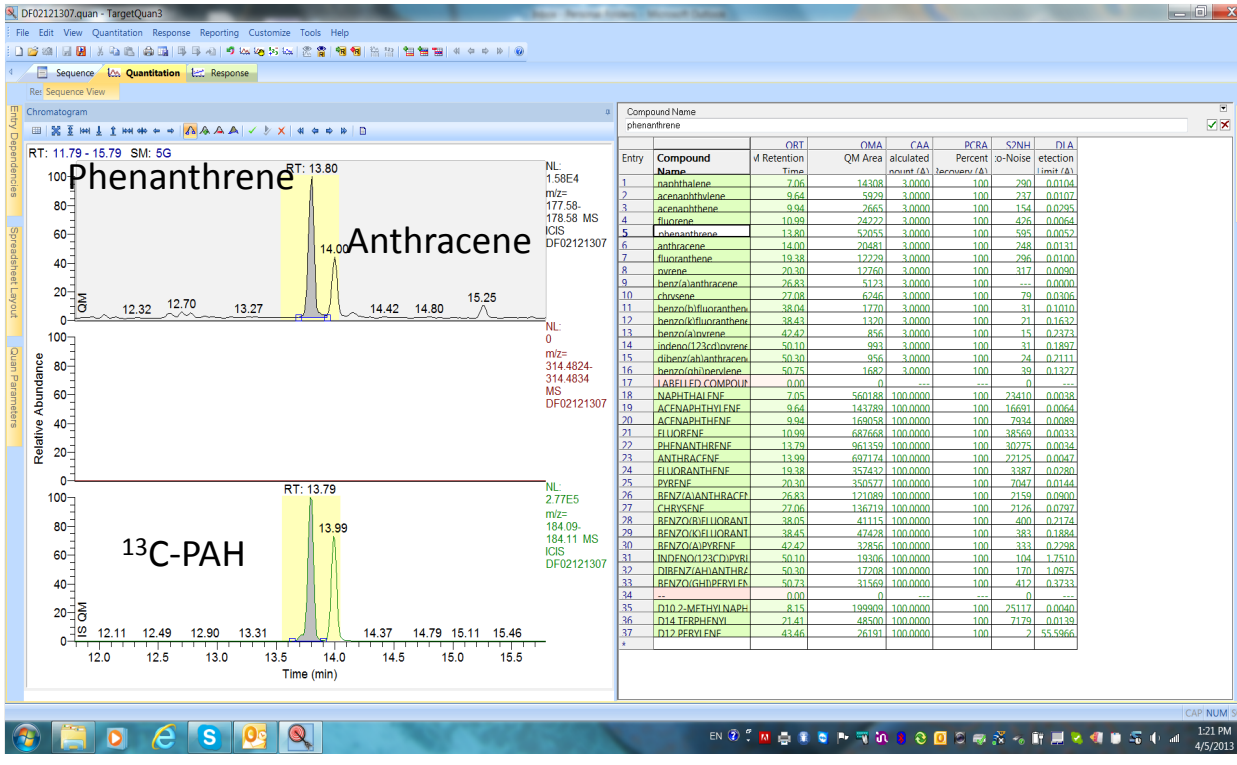
HRMS analysis was the selected for this purpose for its sensitivity. Some 3 pg of phenanthrene and anthracene were injected. Using GC-HRMS analysis, one can see the carbon-13 labeled analogs at 100 pg.

Figure 1: Thermo Scientific DFS Magnetic Sector GC-HRMS.

Tributyltin can also be analyzed via HRMS; using a derivatized deuterated analog of tributyltin, chloride detection limits of <0.001 µg/L or <0.001 mg/kg can be obtained. NDMA (a drinking water contaminant), nonylphenyls, monoethoxylate, and diethoxylate, are also commonly analyzed by HRMS when sensitivity is required. Nonylphenyl is comprised of approximately 20 compounds; with a gross detection limit of 0.01 µg/L, a detection limit of 10–20 times lower is needed for each individual compound.

OCPs are also part of the Stockholm Convention. Traditionally analyzed using an electron capture detector (ECD) or GC-MS, the new EPA 1699 Method of HRMS analysis

Figure 2: Sensitivity not an issue – 3 pg injected (^{13}C-PAH @ 100 pg).



has recently been implemented. The scope of EPA 1699 includes 34 organochlorine pesticides and several carbon-13 standards. In addition, it covers organic pesticides such as triazenes and pyrethroids.

Laboratories commonly use an in-house generated five-point calibration of 1–400 ng/mL with all analytes at the same concentration rather than the varying concentrations listed in EPA 1699. Isotope dilution is used for pesticides that have a carbon-13 labeled standard; internal standards are usually used for everything else. Normally, for HRMS analysis of halogenated compounds, two ions in each parent cluster are monitored; for dioxins and PCBs, the ion ratio should be within 15% of the theoretical. For EPA 1699, ±25% from theoretical is allowed. For sample cleanup, a fluorouracil column elution is split into two or three fractions to focus on a few example analytes at a time, as demonstrated in **Figure 3** for the analysis of Endrin using a mid-level standard at 25 pg/µL and a low-level standard at 1 pg/µL.

New Techniques for HRMS

One of the newest techniques used to improve efficiency in HRMS analyses is the Thermo Scientific DualData XL Module within the DFS Magnetic Sector GC-HRMS. The DFS DualData XL module enables higher throughput and faster response times by staggering injections from two GC

Figure 3: Analysis of Endrin using a mid-level standard at 25 pg/µL and a low-level standard at 1 pg/µL.

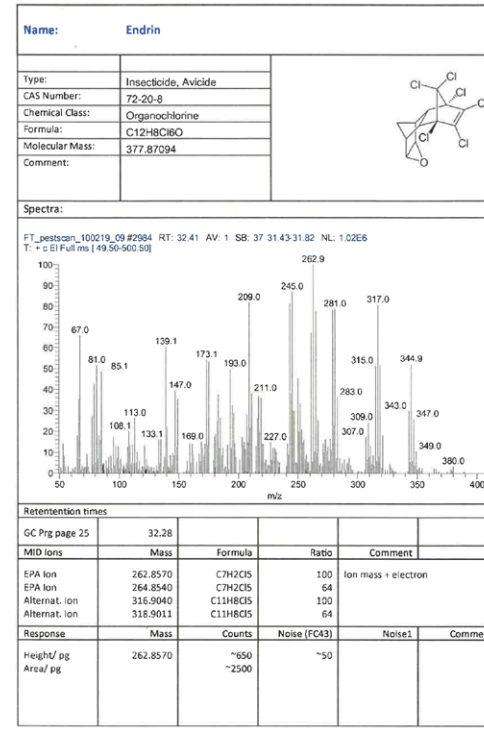


Figure 4: DFS DualData XL module: staggered injection.

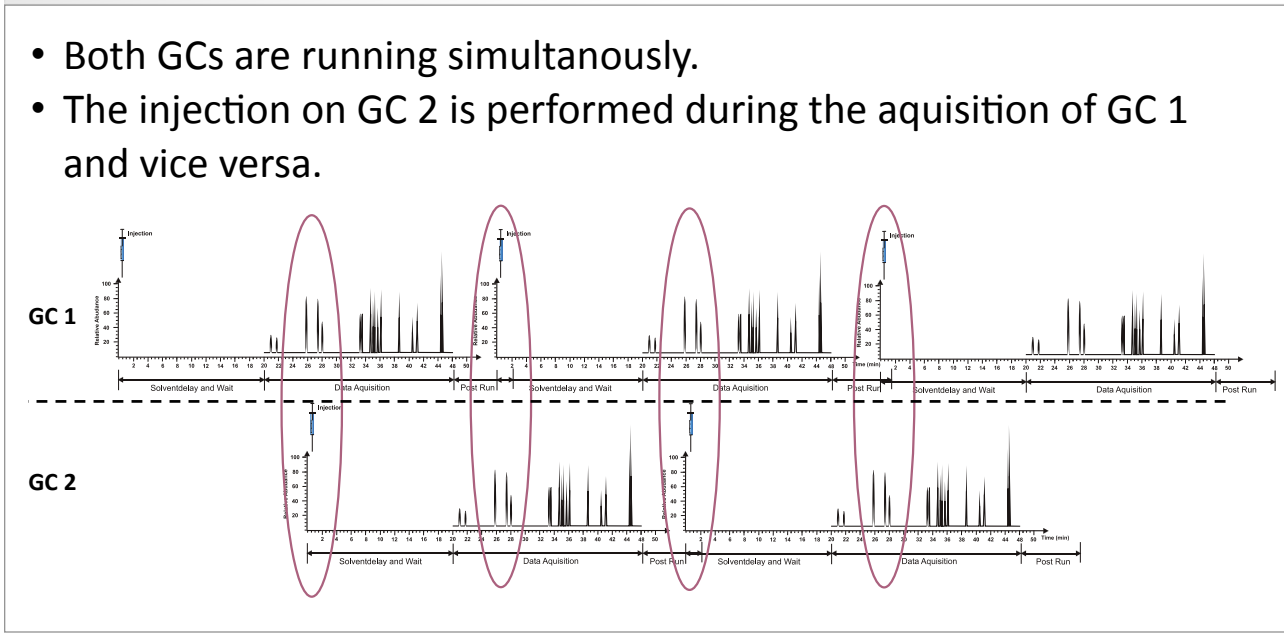
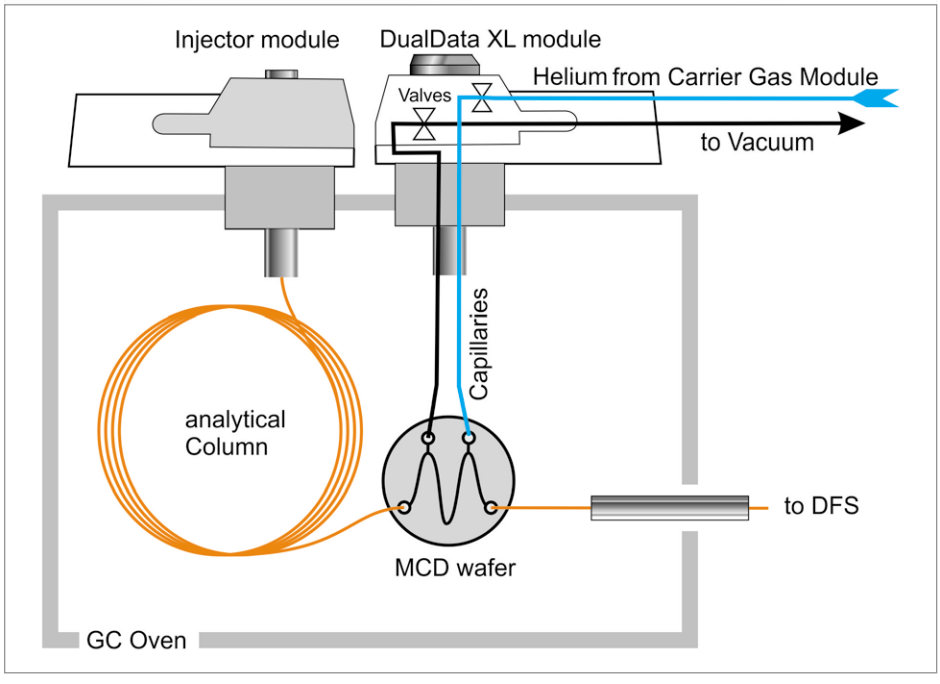


Figure 5: The system also allows for the use of mixed chemistries, all without venting the MS source.



systems to maintain the EPA Method 1613b PCDD required minimum elution time of at least 25 minutes (see **Figure 4**).

The DFS DualData XL mode eliminates the 20-minute wait at the beginning of the analysis by alternating between two GC systems. The second GC instrument injects 20 minutes before the finish of the first GC instrument's run. Then the first GC instrument re-injects 20 minutes before the finish of the second instrument's run. Using a single HRMS system, two GC instruments, and a microwafer, sample throughput can be doubled. The system also allows for the use of mixed chemistries, all without venting the MS source (see **Figure 5**).

For example, with a standard run time of 62 minutes from injection to injection (including cool down and autosampler preparation), the resulting throughput is approximately 23 samples per day. But by running in the DFS DualData XL mode and eliminating the 20-minute offset at the beginning of each run, it takes 67 minutes to complete the cycles for both GC instruments, or approximately 42 injections per day (82% more samples). Other advantages of this module is that it is less expensive than buying a new instrument, it requires no additional floor space, does not require any additional electrical considerations, and the autosampler is ready to inject as soon as a ready signal is established.

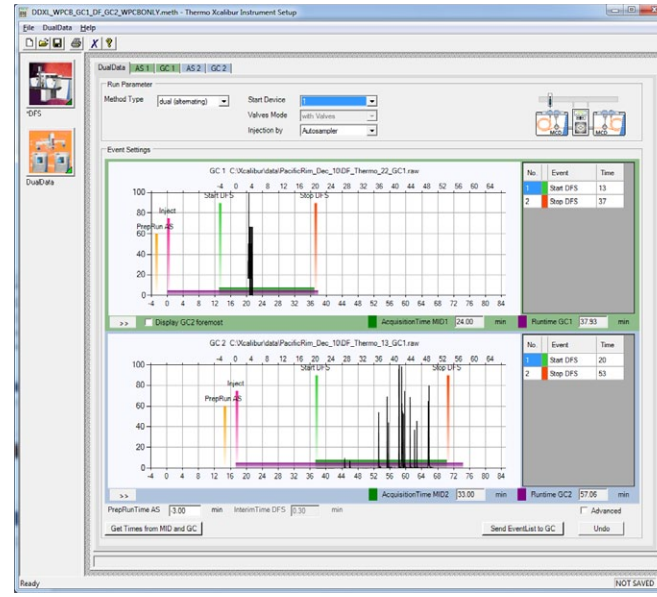
Another DFS DualData XL module example is presented in **Figure 6** for the analysis of dioxins and PCBs. By combining the analysis of dioxins (62 minutes run time) and dioxin-like PCBs (48 minute run time), the DFS DualData XL module run time is only 57 minutes, which is less time

Figure 6: DFS DualData XL module example for the analysis of dioxins and PCBs.

PCDD/F & dlPCB

- PCDD/F Runtime DFS – 62 minutes
- dlPCB Runtime DFS – 48 minutes
- Runtime DualData XL Module – 57 minutes to complete cycle for both GCs

Therefore, you can run dioxins and PCBs together in less time than it takes to run one dioxin sample!!!



than running a dioxin analysis alone, using the HRMS much more efficiently.

Conclusion

HRMS analysis is a valuable tool for any commercial laboratory; with the DualData XL Module within the DFS Magnetic Sector GC-HRMS, it becomes even more valuable. The DFS DualData XL mode significantly increases laboratory efficiency and diversity, since it is not limited to running the same column or GC program on each GC instrument, and the MS source does not need to be vented when changing columns, capabilities are expanded significantly. In addition, because the burn-off at the end of a dioxin or a PBC run is vented to vacuum and not going onto the source, with the DFS DualData XL mode, the source stays much cleaner, resulting in less down time in cleaning, also improving laboratory efficiency.