TECHNICAL NOTE

DualData XL DFS Magnetic Sector GC-HRMS High Throughput Analysis of Polychlorinated Dioxins/Furans (PCDD/Fs)

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Key Words
Dioxins, DualData XL, Furans, GC-HRMS, High Throughput, Magnetic Sector, Module

Goal

Demonstrate how to increase sample throughput for dioxin/furan analyses by using the DualData XL Acquisition configuration of the Thermo Scientific DFS Magnetic Sector GC-HRMS.

Introduction

Magnetic Sector High Resolution GC-MS is the gold standard for high sensitivity analysis of Dioxins and other POPs. Already for decades it has been proving its proficiency in this field of analysis and thus became the established analysis technique available nowadays in leading Dioxin laboratories throughout the world. Together with technical improvements allowing the routinely detection of low femtogram amounts of highly toxic compounds like 2378-TCDD developments in software tools for instrument control as well as data evaluation have led to strong improvements as forease-of-use and productivity with this analytical technology.

Flexibility

Added to the intrinsic high sensitivity and robustness of a Magnetic Sector High Resolution Mass Spectrometer the attachment of 2 Gas Chromatographs to one single MS strongly increases its flexibility allowing for the maximum exploitation and optimum adaptation to laboratory application requirements of this high performance detection device. Dual column adapters enable the installation of 2 columns within one single GC. In combination with a dual GC setup 2, 3 or a maximum of 4 columns can thus be connected to one single mass spectrometer In this way the analytical system can be constantly prepared to perform different applications like PCDD/F, PCBs, PBDEs, etc. changing automatically between columns within a measurement sequence. In another approach latest technical developments based on a dual GC configuration enable to strongly increase sample throughput.

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Productivity

For all gas chromatographic analyses a certain amount of 'dead' time is an intrinsic part of the measurement. The dead time is the time before the first relevant peak is detected and after the last relevant peak elutes. Accordingly this dead time does not contain relevant analytical information and thus can be seen as wasted time (Figure 1).

Dioxin analyses are typically conducted using 60 m columns that result in run times of 50-60 minutes. The dead time for such analyses can be 20-30 minutes per sample. Over a sample sequence this dead time equates to several hours per day that the average mass spectrometer is effectively idle.

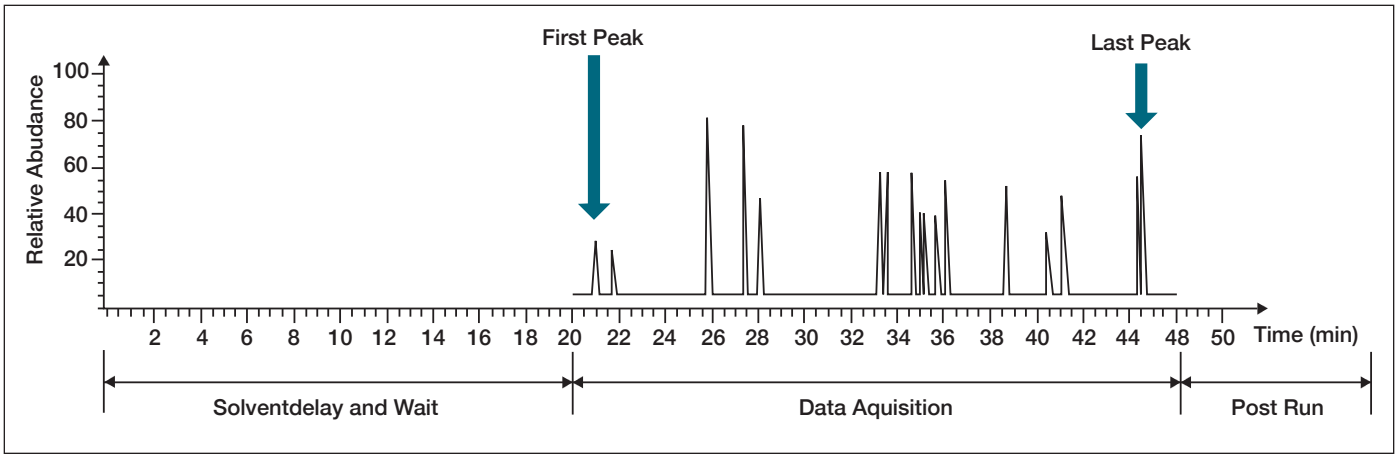


Figure 1. Illustration of waste 'dead' time during a GC-MS analysis.

The chromatographic dead time can be almost eliminated by performing alternate staggered injections using two GCs coupled to a single mass spectrometer (Figure 2). Depending on the ratio between dead time and acquisition time sample throughput can theoretically be doubled. This approach can be used for any type of GC-MS application including combinations of different applications like e.g. Dioxins and PCBs.

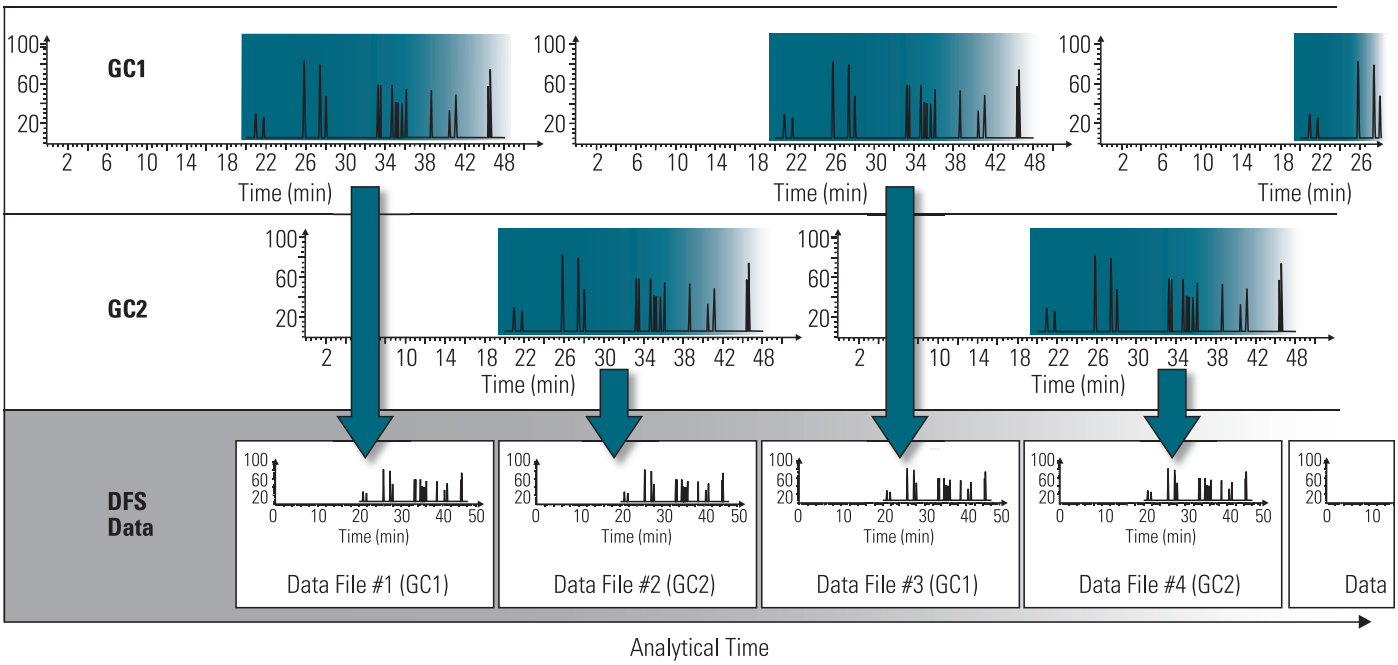
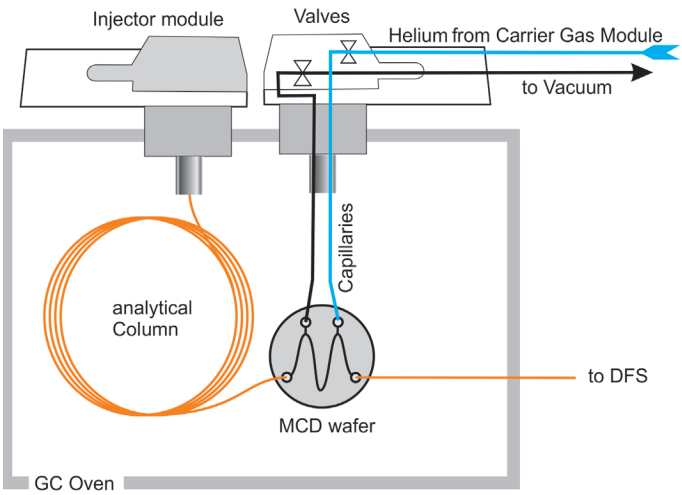


Figure 2. Timescale of a staggered injection sequence using a two GC, single MS configuration.

To realize a staggered injection sequence a hardware modification inside each GC needs to be implemented. This modification needs to ensure that only the flow of one analytical column at a time is guided into the ion source of the mass spectrometer. Therefore a time controlled dynamic flow switching system was developed, implemented in a modular way based on the Thermo Scientific™ TRACE™ 1310 GC (Figure 3b).

By using a proprietary microfluidic channel device (MCD) to switch flow between vacuum purge and MS it is possible to successfully handle the rigors of high throughput POPs analysis, without compromise on sensitivity, chromatography or robustness (Figure 3a).



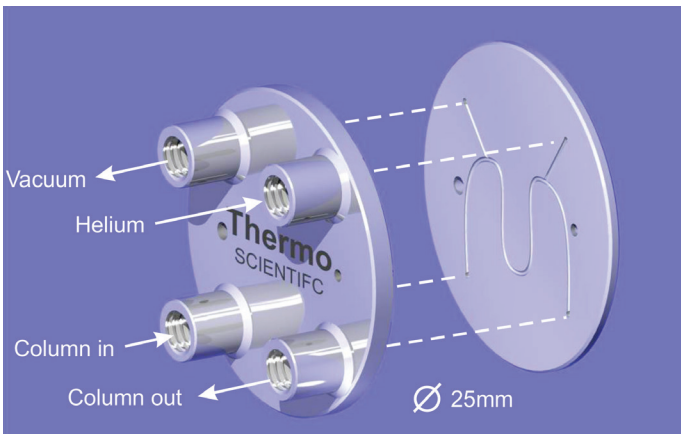


Figure 3a. Principle of the dynamic flow switching system of the DualData XL DFS GC-HRMS (left) and inner view of a micro fluidic channel device (MCD) wafer (right).

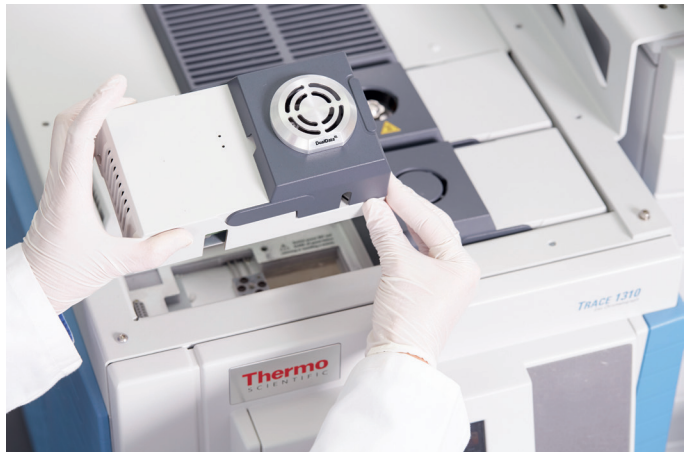


Figure 3b. DualData XL Module on a Thermo Scientific TRACE 1310 GC.

In a typical experiment, the first GC run was started, and during the wait time of 20 minutes, while the solvent peak as well as other compounds of no interest eluted all GC eluate was diverted to waste. After 20 minutes, the GC eluate was directed to the ion source of the MS and MS data acquisition started. At approximately the same time, a second sample was injected to the second GC, running the same process as the first one. (i.e. during the first 20 minutes no GC eluate was directed towards the MS. Once the first GC finished cooling down the oven to start condition, another injection occurred, and the same scheme as denoted above repeats). This resulted in two GCs running simultaneously with staggered sample injections. Only the retention time windows of interest from each GC were directed to the MS for data acquisition.

Methods

The configuration used consists of two Thermo Scientific TRACE 1310 GC equipped with the DualData XL Module using two columns coupled to the Thermo Scientific™ DFS™ Magnetic Sector GC-HRMS. The mass spectrometer was set up in a multiple ion detection mode (MID) at a resolution of 10,000 (10% valley definition). FC43 and PFK was used as a reference compound to provide the inherent lock and cali masses. The Thermo Scientific™ TriPlus RSH Autosampler with extended x-rail served both GCs from one common sample tray. Typically one µL of sample was injected. A method 1613 CS1 – CS5 calibration standard (1:10 diluted from Cambridge Isotope Laboratories) and CS3 / CPM 8290/1613 was used as well as EPA method 1668 and 1614 standards to demonstrate the chromatographic performance of the system. A low level pooled blood sample in the range of 20fg/ml of 2,3,7,8 TCDD in dirty matrix was also used to demonstrate the performance in terms of sensitivity.

Results

Performance: The analytical performance with DualData XL Acquisition and conventional GC-MS configuration was compared using the same set of polychlorinated dioxins and furans, PCBs and PBDE samples as model compounds
(Figure 4).

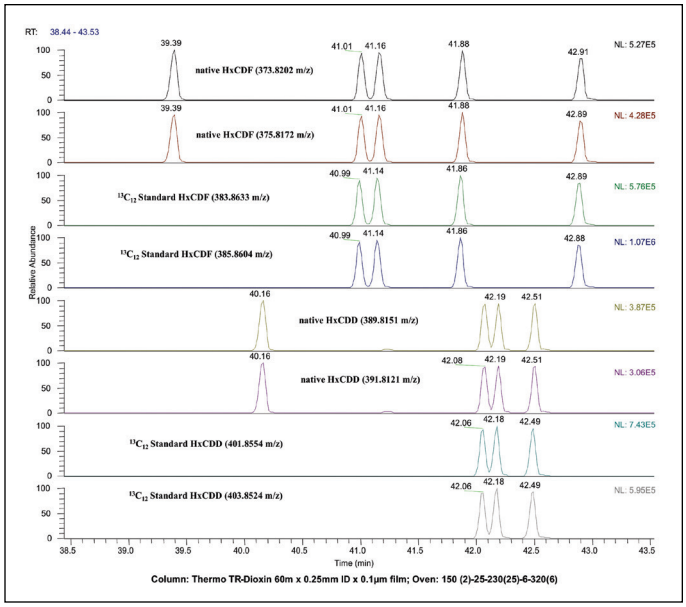


Figure 4. Example of peak integrity of Dioxin trace analysis (Hexa CDD/F) using the DualData XL Acquisition.

Sensitivity was compared by using low concentrated PCDD/PCDF standards as well as a low level pooled blood sample (Figure 5).

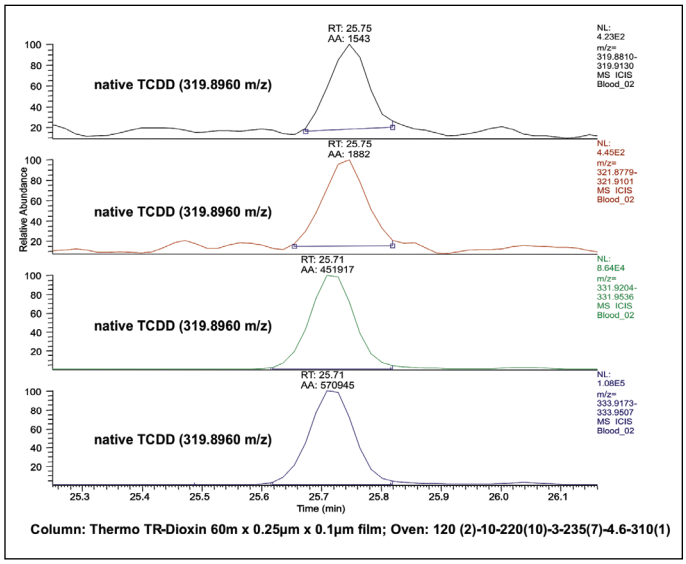


Figure 5. 1 µl Blood sample in dirty matrix in the range of 20 fg/µl TCDD.

It was found that the effects due to some increased dead volumes and a disturbed flow path caused by the MCD were negligible. No additional peak tailing was observed and the requirements of EPA method 1613 to separate the 2,3,7,8 TCDD to the next eluting TCDD with a valley of better than 25% was easy achievable (Figure 6).

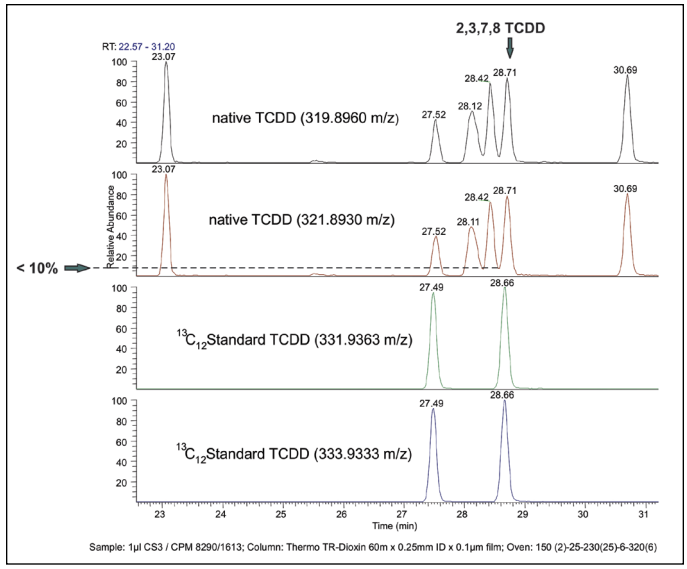


Figure 6. Separation of the 2,3,7,8-TCDD to the next eluting TCDD. The valley is below 25% as requiered by EPA1613.

Flexibility: Also other POPs such as PCBs and PBDEs can be run with the DualData XL Module as well as combinations of different applications per GC on one DualData XL Module. (e.g. Dioxins on GC1 60m column and PBDEs on GC2 using a 15m column).

Productivity: The amount of samples running a staggered Sequence of dioxin and furan analysis using DualData XL Module was compared to a standard dual GC configuration. The analysis was done on Thermo Scientific TR-Dioxin 60 m x 0.25 mm ID x 0.25 µm film in each GC with a total runtime of 43 min. The acquisition was started after 20 min. In standard dual GC mode 16 samples were analyzed compared to 32 samples with the DualData XL Module during a time frame of 12 hours.

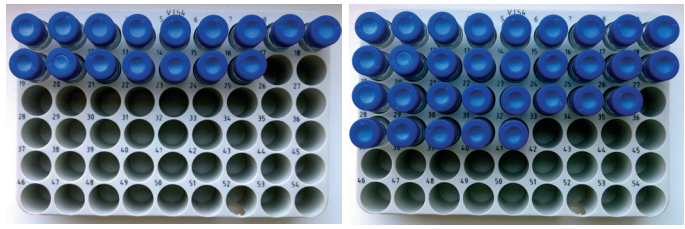


Figure 7. Sample throughput in a timeframe of 12 hours. In standard dual GC configuration 16 Samples (left) were measured compared to 32 samples with the DualData XL Module (right).

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Conclusion

It has been demonstrated that the DualData XL Module for the DFS Magnetic Sector GC-HRMS allows a higher sample throughput by no loss in performance such as peak shape or sensitivity. The GC separation integrity, ruggedness and long-term stability of the column switching system have been proven in unattended sample.

- Increase of productivity up to double sample throughput.
- Excellent peak shape using MCD wafer technology.
- No loss in sensitivity compared to a standard dual GC System.
- Applicable to different POPs such as Dioxins, PCBs and PBDEs.

References

1. U.S. Environmental Protection Agency, Method EPA 1613 Rev. B, Washington, October 1994.
2. European Committee for Standardization, EN 1948, Brussels, December 1996.
3. Application Note AN30098, Thermo Fisher Scientific, Bremen 2006.

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