Maximized productivity for PBDE, Dioxin and PCB analysis using DualData Mode with Magnetic Sector GC-HRMS

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ABSTRACT

Purpose: Added to the intrinsic high sensitivity and robustness - due to the large ion source - for Dioxin and POPs analysis of a Magnetic Sector High Resolution Mass Spectrometer the attachment of 2 GCs to one single MS strongly increases its flexibility (Figure 1a). Furthermore on the basis of such a Dual GC Magnetic Sector Mass Spectrometer the concept of DualData XL acquisition was developed (Figure 1b). This concept and its technical implementation allow to strongly increase the sample throughput. Effectively the productivity in number of samples injected on one single MS is almost doubled.

FIGURE 1a. Thermo Scientific DFS Magnetic Sector GC High Resolution Mass Spectrometer coupled to two Thermo Scientific TRACE 1310 GC.

Methods: 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. 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 up to 20-30 minutes per sample.

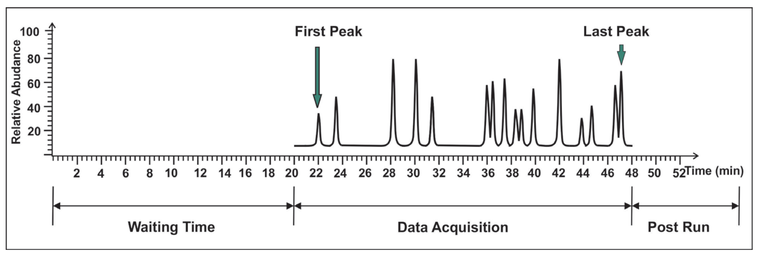


FIGURE 2. Timescale of a typical dioxin analysis.

The dead time can be almost eliminated by performing alternate staggered injections using two GCs coupled to one MS. First of all both GCs are running in parallel. Secondly the timing is such that the chromatogram section with peaks from one GC falls into the chromatogram section with no peaks from the other GC and vice versa. To realize a time-controlled staggered injection sample sequence specific software is needed and some hardware modifications inside of each GC need to be implemented. These modifications ensure that at any point of time the flow of one GC only – time section with peaks - is guided into the mass spectrometer for measurement while the flow of the other GC – time section without peaks - is directed into waste. A time controlled dynamic flow switching system was developed using a proprietary micro fluidic channel device (MCD) to switch flow between vacuum purge and MS (see Figure 4).

Results: Chromatograms with and without the MCD device are practically undistinguishable from one another in terms of peak shape or sensitivity. The concept was proven by numerous experiments and is by now validated in full production dioxin analysis laboratories. The Thermo Scientific DualData XL Module for the Thermo Scientific™ DFS™ Magnetic Sector GC-HRMS can be used for a range of POPs analyses applications such as Dioxins, PCBs or PBDEs. Also a combination of different applications is possible. With an increase of more than 90% the sample throughput for e.g. Dioxins is almost doubled.

INTRODUCTION

The sequence timeline on a standard dual GC configuration is interrupted by segments of dead time (see Figure 3a). In the sequence timeline of a DualData XL Module equipped dual GC configuration a staggered injection is possible with no dead time between each data acquisition (see Figure 3b).

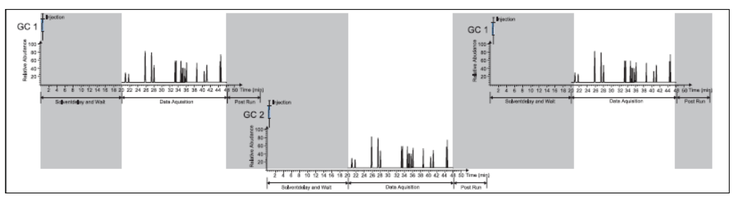


FIGURE 3a. Normal dual GC configuration: The gray area represents dead time, where no data is acquired.

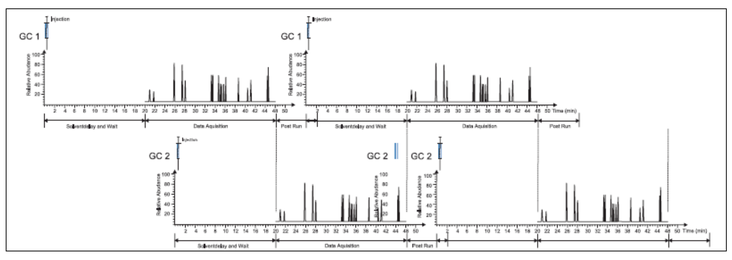


FIGURE 3b. DualData XL acquisition sequence. Only the relevant retention time windows of both GCs are monitored.

Each GC was equipped with a dynamic flow switching system which allows to divide the GC eluate to waste or to the MS source (see Figure 4). The ability to cut out parts of the chromatogram in order to prevent any cross contamination caused by the second GC run was checked by a measurement of a EPA 1613 CS5 standard. Furthermore the ability to cut out the solvent was proved by monitoring the MS Ion source pressure while injection solvent up to a volume of 10ul into the system. The solvent don't reach the source, when the valves are in ON position. In the meantime the flow into the ion source will be compensated by He delivered by a computer controllable carrier gas module in order to keep the pressure in the ion source constant .

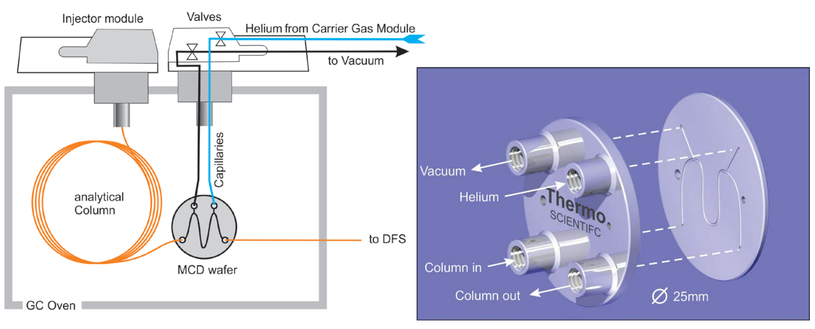


FIGURE 4. Principle of the dynamic flow switching system of the DFS GC-HRMS DualData XL Module (left) and inner view of a micro fluidic channel device (MCD) wafer (right).

FIGURE 1b. 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. Figure 5 illustrates the measurement sequence from both of the GCs providing consecutive data files for target compound quantification.

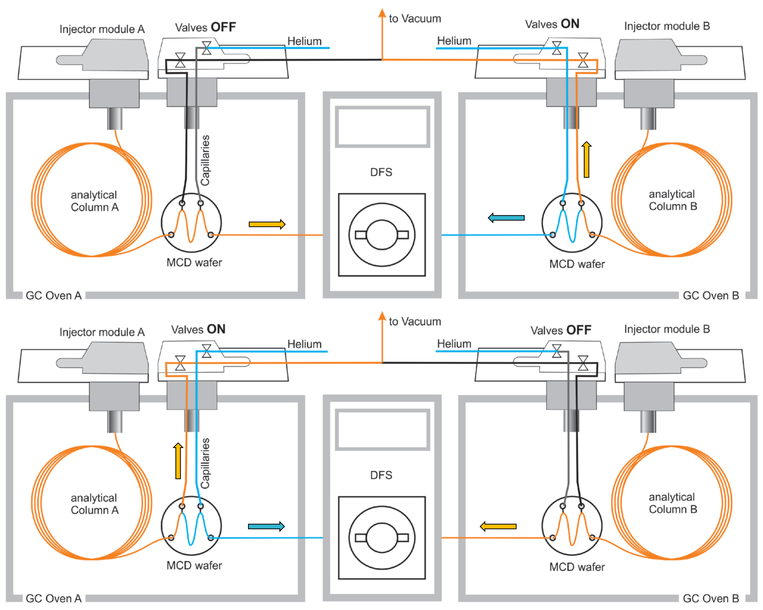


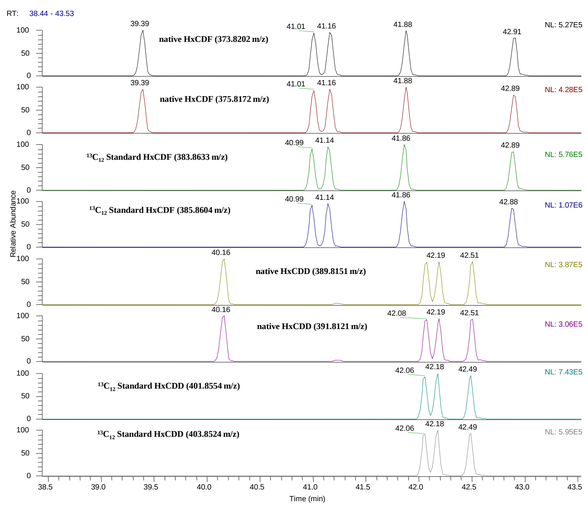
FIGURE 5. Flow of the analytical column of GC A is guided into the MS and is acquired while the flow of GC B is directed into waste (upper schematic) and vice versa (lower schematic).

MATERIALS AND METHODS

The configuration used in this study 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 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 used to demonstrate the performance in terms of sensitivity.

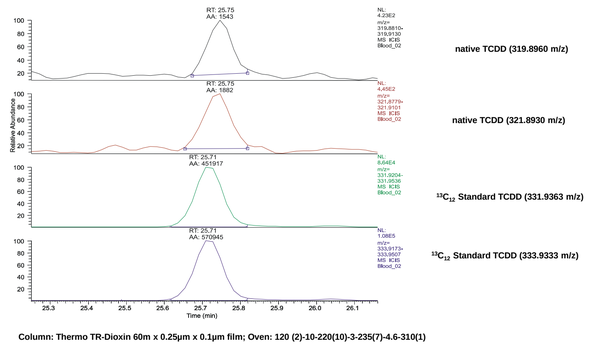
RESULTS

Performance: The analytical performance with DualData XL Module and conventional GC/MS configuration was compared using the same set of polychlorinated dioxins and furans, PCBs and PBDE samples as model compounds. Sensitivity was compared by using low concentrated PCDD/PCDF standards as well as a low level pooled blood sample. The GC separation integrity, ruggedness and long-term stability of the column switching system have been proven in unattended sample.



Column: Thermo TR-Dioxin 60m x 0.25mm ID x 0.1µm film; Oven: 150 (2)-25-230(25)-6-320(6)

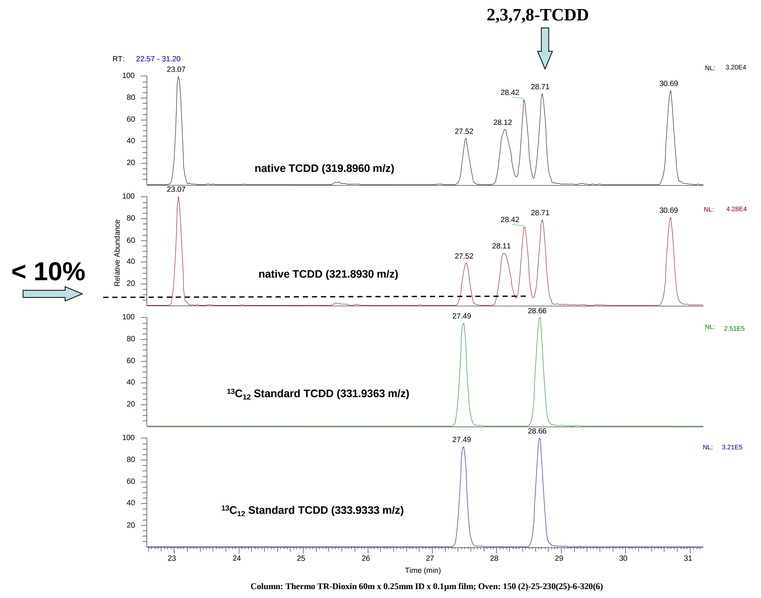
FIGURE 6a. Example of peak integrity of Dioxin trace analysis (Hexa CDD/F) using the Dual Data Acquisition.



Column: Thermo TR-Dioxin 60m x 0.25µm x 0.1µm film; Oven: 120 (2)-10-220(10)-3-235(7)-4.6-310(1)

FIGURE 6b. 1µl Blood sample in dirty matrix in the range of 20 fg/µl TCDD.

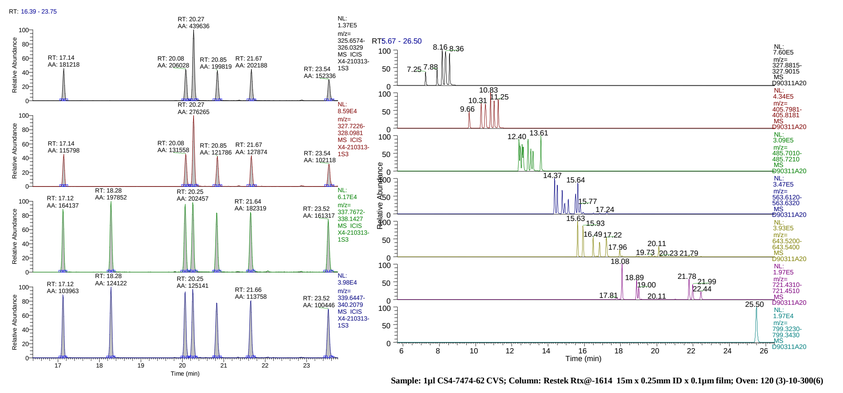
It was found that the effects due to some increased dead volumes and a disturbed flow path caused by the MCD were negligible. No additional peak tailing was observed and the requirements of EPA 1613 to separate the 2,3,7,8 TCDD to the next eluting TCDD with a valley of better than 25% was easy achievable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



Column: Thermo TR-Dioxin 60m x 0.25mm ID x 0.1µm film; Oven: 150 (2)-25-230(25)-6-320(6)

FIGURE 7a. 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 Dual Data option as well as combinations of different applications per GC on one Dual Data System. (e.g. Dioxins on GC1 60m column and PBDEs on GC2 using a 15m column)



Sample: 1µl CS4-7474-62 CVS; Column: Restek Rtx@-1614 15m x 0.25mm ID x 0.1µm film; Oven: 120 (3)-10-300(6)

FIGURE 8. Example of PCB trace analysis (5Cl PCB) (left). Example of PBDEs trace analysis (right).

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

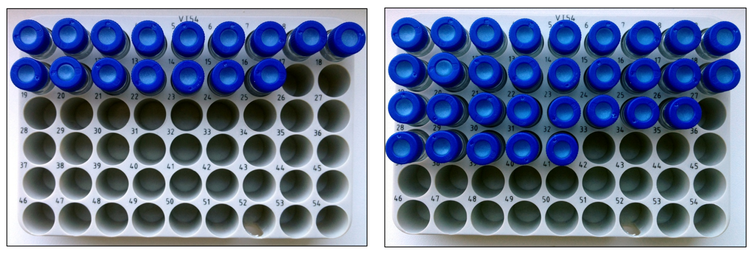


FIGURE 9. Sample throughput in a timeframe of 12 hours. In standard dual GC configuration 16 samples (left) were measured compared to 32 samples with the DualData XL Module (right).

Conclusion

It has been demonstrated that the Dual Data option allows a higher sample throughput by no loss in performance such as peak shape or sensitivity.

- 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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