Application Note: 30174

Dual Data Acquisition for High Throughput Analysis of Polychlorinated Dioxins/Furans (PCDD/Fs)

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Key Words

- DFS
- Dioxins
- High Throughput
- Dual Data Acquisition
- Furans
- HRGC/HRMS

Introduction

Analysis of dioxins and furans (PCDD's/PCDF's) in accordance with EPA1613 or EN1948 takes a GC cycle time of some 45-60 minutes. During this cycle, only the time between the first and last eluting analyte compounds is of analytical interest, the rest is idle time (see Figure 1). The Dual Data Acquisition option is a hardware modification based on a Dual GC-Single MS configuration. It enables alternating injection series into both GCs which allows both GCs to alternately show data between the first and last eluting analyte, leading to increase of the number of HRMS duty cycles and a subsequent increase in productivity. One dual-GC single-MS system, equipped with the Dual Data Acquisition option, has a comparable sample throughput of two single GC-MS systems.

Materials and Methods

The configuration used in this study consists of two GCs (Thermo Scientific TRACE GC Ultra) equipped with two split/splitless injectors and two identical columns (Thermo Scientific TR-Dioxin, 60 m, 0.25 mm ID, 0.25 µm film thickness) coupled to high resolution magnetic sector GC/MS instrument (Thermo Scientific DFS).

The mass spectrometer was set up in a multiple ion detection mode (MID)[1] at a resolution of 10,000 (10% valley definition). FC43 was used as a reference compound to provide the inherent lock and cali masses. For MID Method Setup refer to Application Note 30112.[2] The same oven program: 120 (2)-10-220(10)-3-235(7)-4.6-310(1) was applied to both GCs. The autosampler used was a Thermo Scientific TriPlus XT model with extended x-rail for serving both GCs from one common sample tray.

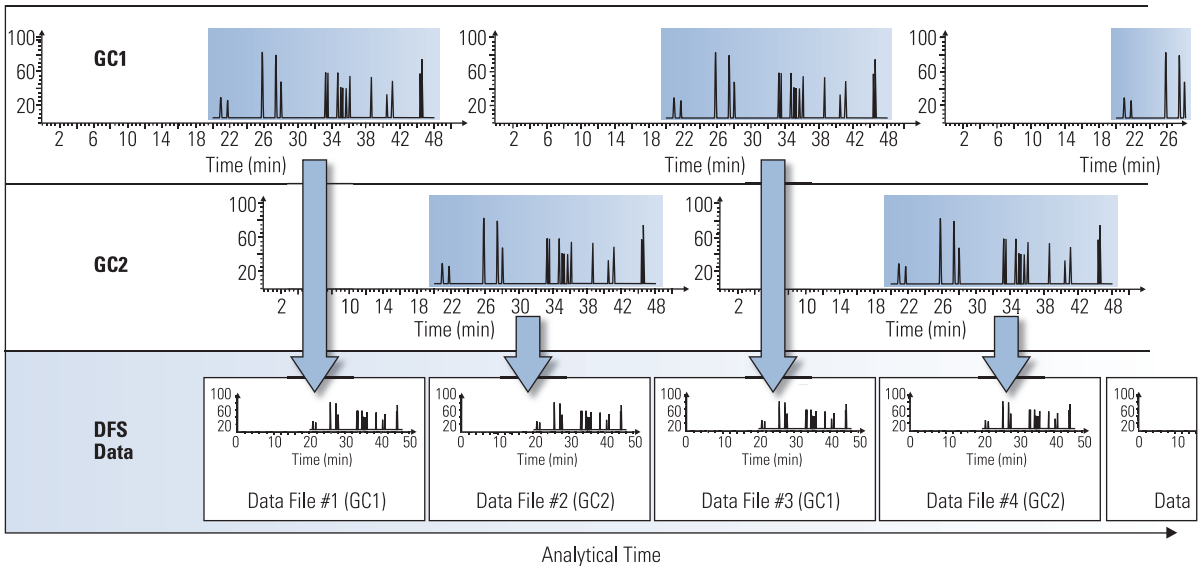

Figure 1: A staggered injection minimizes the waiting time between data acquisition windows and generates a continuously dataflow.

Typically one µL of sample was injected using the hot needle injection technique. A method 1613 CS1 – CS5 calibration standard (1:10 diluted, 50 fg - 20 pg TCDD, Cambridge Isotope Laboratories Inc., Andover, MA, USA) was used to check the system performance in terms of sensitivity, linearity and repeatability. The column of each GC was directed into the ion source by direct coupling. Each GC was equipped with a dynamic flow switching system which allows to direct the GC eluate to waste or to the MS Source (see Figure 2).

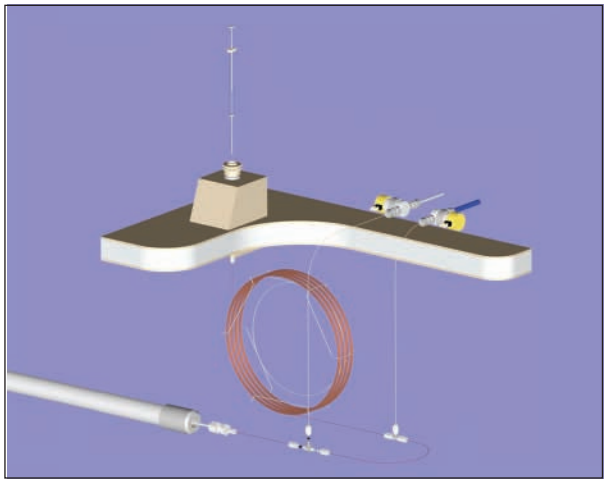

Figure 2: Principle of the DFS Dual Data Acquisition column switching system for dynamic flow switching of the GC effluent.

Results

In a typical Dual Data experiment, the first GC run is started, and during the first 20 minutes, while the solvent peak as well as other compounds elute, all GC eluate is diverted to waste. After 20 minutes, the GC eluate is directed to the ion source of the MS and MS data acquisition starts. At approximately the same time, a second sample is injected on the second GC, and again, during the first 20 minutes, while the eluate of the first GC is directed to the MS, no eluate from the second GC is directed to the MS, but directed to waste. (i.e. during the first 20 minutes no GC eluate is directed towards the MS. Once the first GC oven finishes cooling down to start conditions, another injection occurs, and the same cycle starts again). This results in two GCs running simultaneously with staggered sample injections. Only the retention time windows of interest from each GC are directed to the MS for data acquisition. Figure 3 illustrates the measurement sequence from both of the GCs providing consecutive data files for target compound quantification.

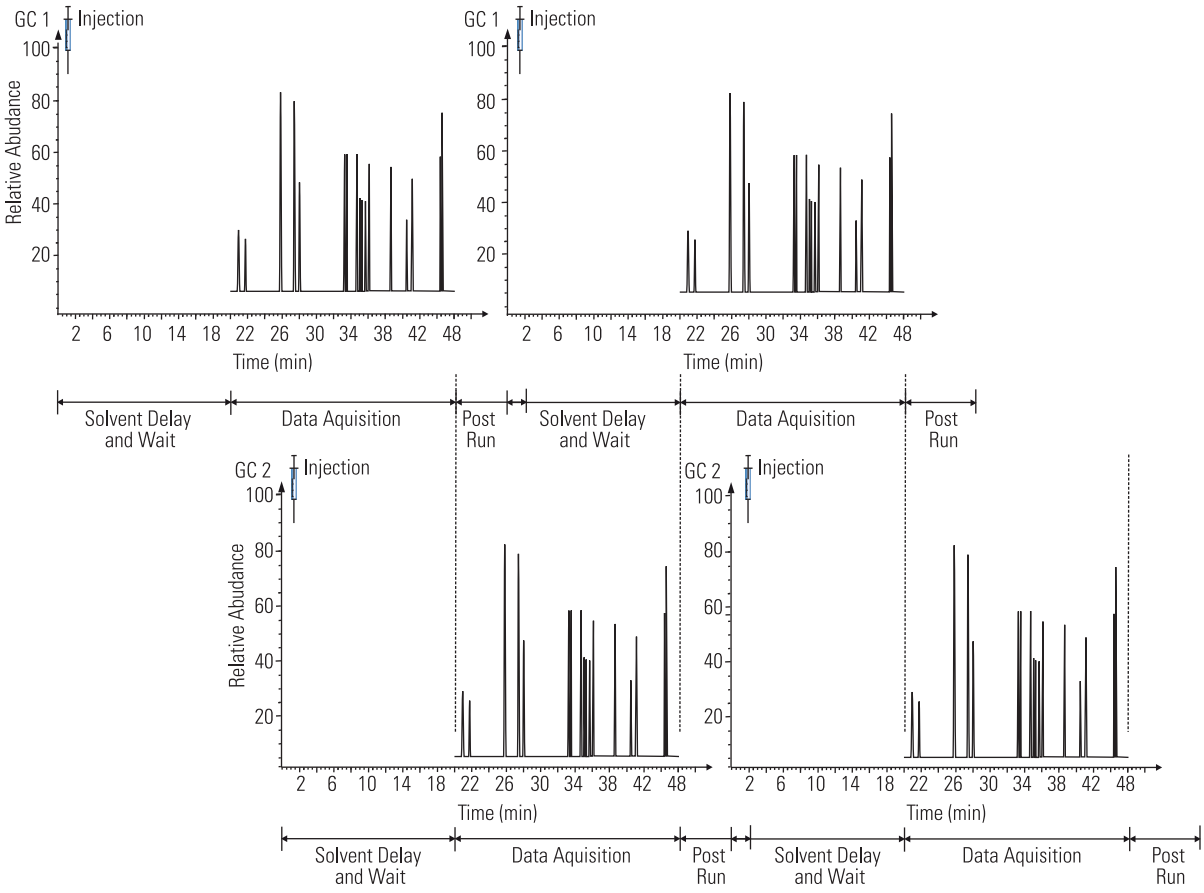

Figure 3: Dual Data Acquisition sequence. Only the relevant retention time windows of both GCs are monitored e.g. for dioxin/furan analysis by the MS.

The ability to cut out parts of the chromatogram in order to prevent any cross-contamination caused by the second GC run is demonstrated by a measurement of a high concentrated standard (CS5, see Figure 4a and 4b). In a similar experiment it was shown, that the sample solvent up to volumes of 10 µl and more can be directed completely into waste.

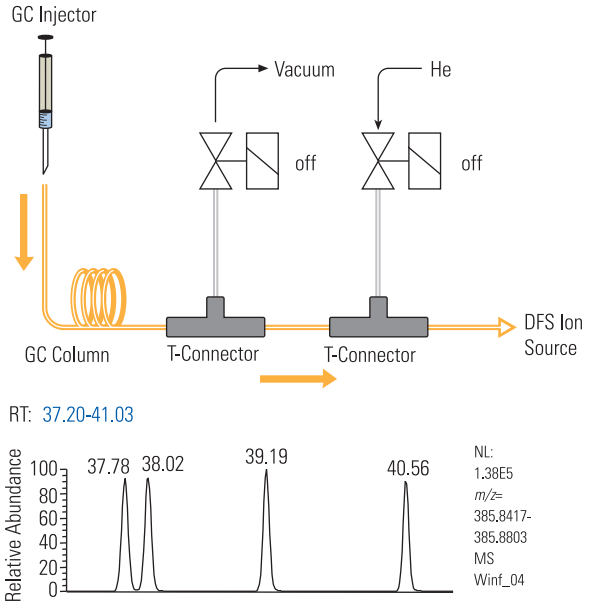

Figure 4a: Directing the eluate into the source.

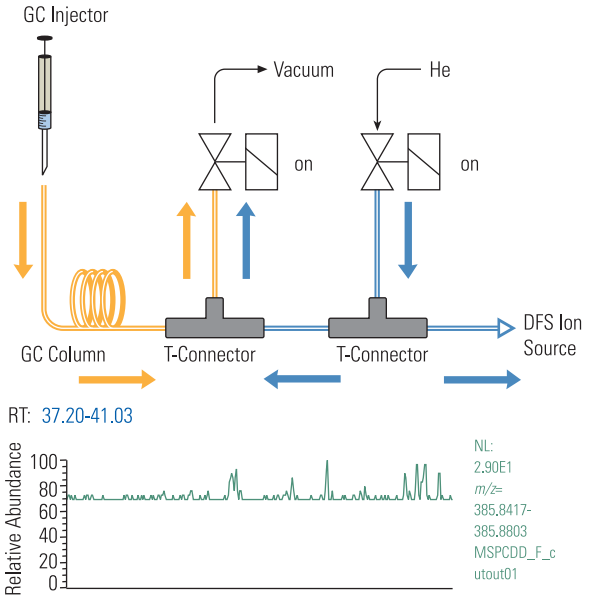

Figure 4b: Directing the eluate into waste.

The analytical performance with Dual Data Acquisition and conventional GC/MS configuration was compared using the same set of polychlorinated dioxin and furan samples as model compounds. It was found that possible effects due to increased dead volumes and a disturbed flow path caused by the connectors and valves were negligible. Sensitivity was compared by using low concentrated PCDD/PCDF standards. The GC separation integrity, ruggedness and long-term stability of the column switching system have been proven in unattended sample runs (see Figure 5a and 5b).

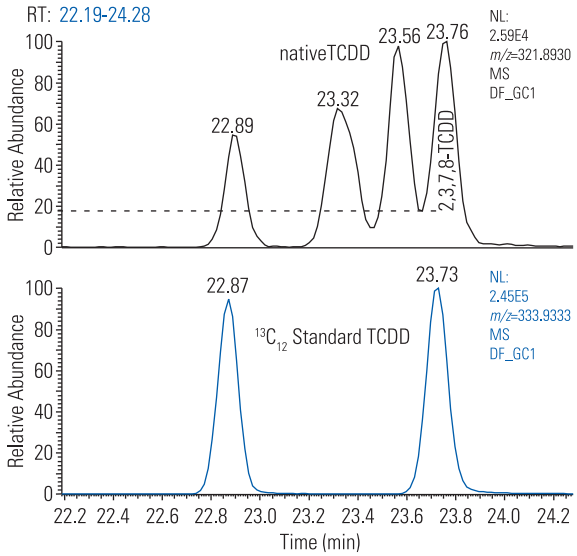

Figure 5a: The separation of 2,3,7,8-TCDD from most closely eluted isomers is below 25% Valley, according to EPA 1613.[3]

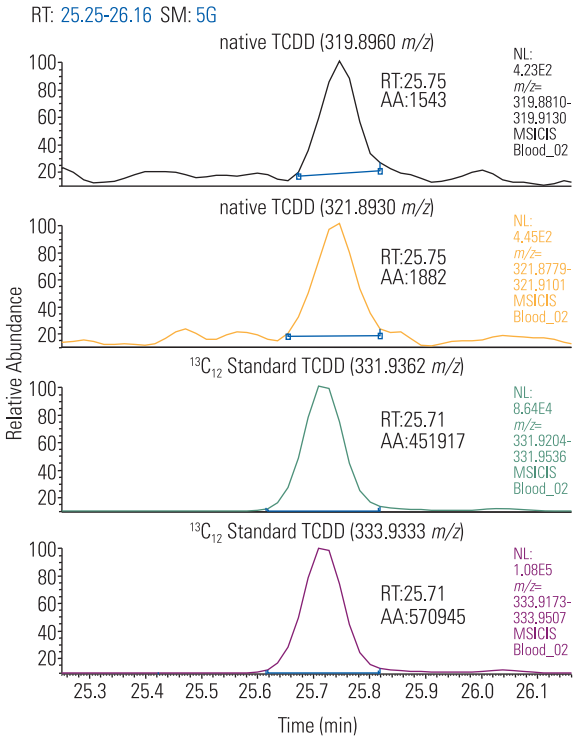

Figure 5b: Blood sample in dirty matrix in the range of 20 fg/µl TCDD. Sample: 1 µl blood; Column: TR-Dioxin 60 m x 0.25 µm x 0.1 µm film; Oven: 120 (2)-10-220(10)-3-235(7)-4.6-310(1).

Conclusions

The sample throughput for dioxin/furan analyses with typical cycle times of up to 60 minutes can be nearly doubled by using the Dual Data Acquisition configuration. Using this setup selective exclusion of parts of the chromatogram could be accomplished to achieve a continuous dataflow. Effects due to some increased dead volumes and a disturbed flow path caused by the connectors and valves are negligible. Performance in terms of peak shape, separation and sensitivity is comparable with a single GC-HRMS system. As a positive side effect the matrix load to the MS is reduced by directing the eluate during the heat-out phase of each GC run to waste.

References

[1] Hans-Joachim Huebschmann, Jens Griep-Raming, High Resolution MID Data Acquisition for Target Compound Analysis with the DFS GC/MS System, Thermo Fisher Scientific Technical Note: 30116

[2] Dirk Krumwiede, Hans-Joachim Huebschmann, Confirmation of Low Level Dioxins and furans in Dirty Matrix Samples using High Resolution GC/MS, Thermo Fischer Scientific Application Note: 30112

[3] Method 1613 Rev.B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, U.S. Environmental Protection Agency Office of Water Engineering and Analysis Division, Washington, Oct. 1994

Thermo Scientific Application Components

Description	Part Number
TR-Dioxin GC Column 60 m x 0.25 mm x 0.25 µm	26AF154P
S/SL Liner, 5 mm ID, 105 mm, 5 pk	45350033
Graphite Liner Sealing Ring, 10 pk	29033406
Graphite/Vespel Ferrules, 0.1-0.25 mm (Injector)	290VT186
Graphite/Vespel Ferrules, 0.1-0.25 mm (GCMS)	29033496
10µL FN Syringe, 50 mm, 25	36500525
BTO Injection Port Septa, 50 pk	31303211

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