INCREASING PRODUCTIVITY OF POPs ANALYSIS ON A SINGLE MASS SPECTROMETER USING MICRO-FLUIDIC CHANNEL DEVICE WAFERS

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Introduction

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. This dead time is wasted because no analyte measurement is performed during this period.

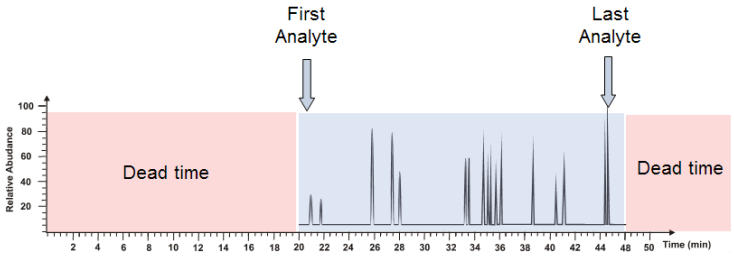

Figure 1. Illustration of waste 'dead' time during a GCMS analysis

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.

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

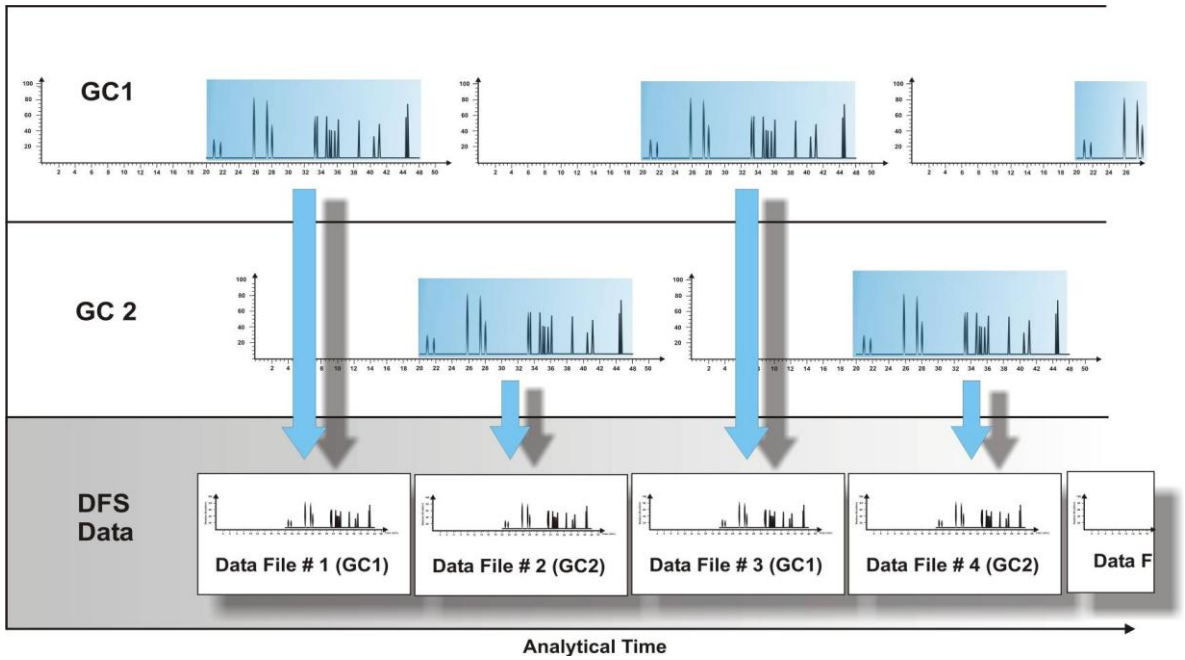

Figure 2. Timescale of a staggered injection sequence using a two GC, single MS configuration.

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 using a proprietary microfluidic channel device (MCD) to switch flow between vacuum purge and MS.

The device, Figure 3, was able to successfully handle the rigors of high throughput POPs analysis, without compromise on sensitivity, chromatography or robustness.

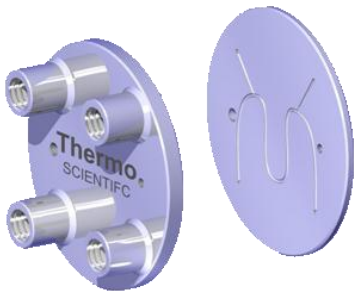

Figure 3. Proprietary microfluidic channel device (MCD)

Materials and methods

The Thermo Scientific™ DualData Generation 2 system comprised of:

- DualData G2 valves and MCD wafers.
- Two Thermo Scientific Trace Ultra™ GCs
- A single Thermo Scientific DFS™ high resolution mass spectrometer
- Thermo Scientific TriPlus™ XT auto sampler
- Thermo Scientific DualData & Xcalibur™ 2.0 software to control switching events and data acquisition.

A time controlled dynamic flow switching system was developed and implemented into each GC. With this system the flow of the analytical column can be either directed into the mass spectrometer for detection or into a vacuum purge line. A regulated helium gas supply was used as makeup gas which compensates the flow into the MS when the analytical column flow is guided into the service vacuum. Helium and vacuum lines were controlled by switching valves mounted on the GC top (Figure 3.). All restrictions and connections inside the GC oven are implemented on a miniaturized MCD.

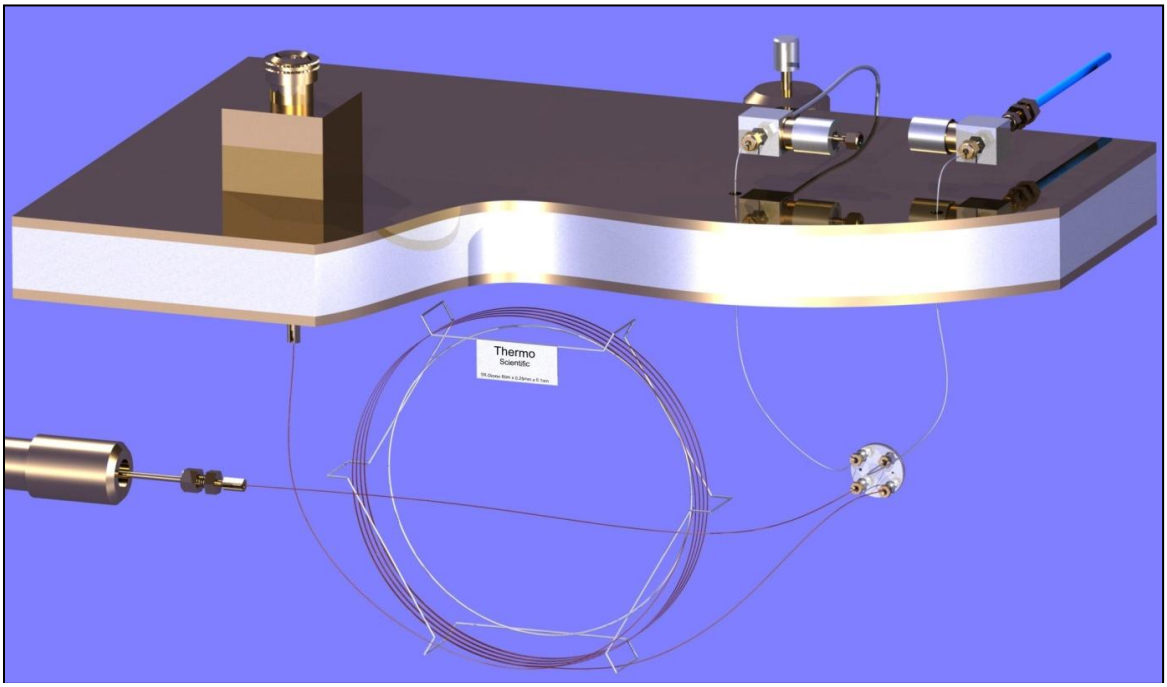

Figure 3. The DualData Generation 2 flow switching system with MCD, switching valves and helium regulator was installed into each GC.

Timing control for all sequence events was implemented inside the instrument experiment method file. Each data file contained the full information of instrument parameters of the GC, HRMS and auto-sampler. The retention time of the acquired data is synchronized with the GC run time.

Analysis of Dioxins, PCBs and PBDEs were tested using both standards and sample extracts under regulated analysis conditions; such as EPA 1613 B for Dioxin analysis[1]. Also combinations of different applications per GC were performed.

Results and discussion

During hardware development the primary focus was to ensure robustness, ease of use and analytical performance of the DualData Generation 2 system. The concept was proven by numerous experiments and again validated in full production dioxin analysis using >1200 samples at a leading contract testing laboratory in Hamburg, Germany. The system as described here was tested to be able to cut out even high concentrated standards and demonstrated to work in routine with large injection volumes of 10 µL and higher. Even with large injection volumes, no solvent was found to reach the mass spectrometer, proving the 100% performance of the MCD device to switch column flow to vacuum. This gives absolute assurance that peaks from only one GC at any given point of time can reach the MS for detection.

Using the new MCD wafer resulted in many benefits compared to previous approaches with different flow switching hardware:

- **Low thermal mass** – enabling exceptional chromatography even for high boiling analytes such as BFRs
- **Exceptionally low dead volume** – giving chromatography indistinguishable from a standard GC experiment
- **Fewer unions** – enhancing robustness, minimizing leaks and simplifying operation and handling.
- **Simple unions** – making the system easier to install and maintain, to maximize your productivity.
- **Special inert coating** - increasing the robustness and longevity of the unions when compared to previous 'T' connectors.
- **Column fitting tool** - to ensure simple low dead volume column installation without requirement of complex alignment.
- **Helium flow restrictors** are now implemented within the wafer. This precision milled channels deliver perfect flow restriction and the MCDs are practically unbreakable, unlike conventional capillary flow restrictors.

Chromatograms with and without this wafer are undistinguishable from one another in terms of peak shape or sensitivity (Figure 4). The connection between column and wafer are leak tight even after more than one thousand injections.

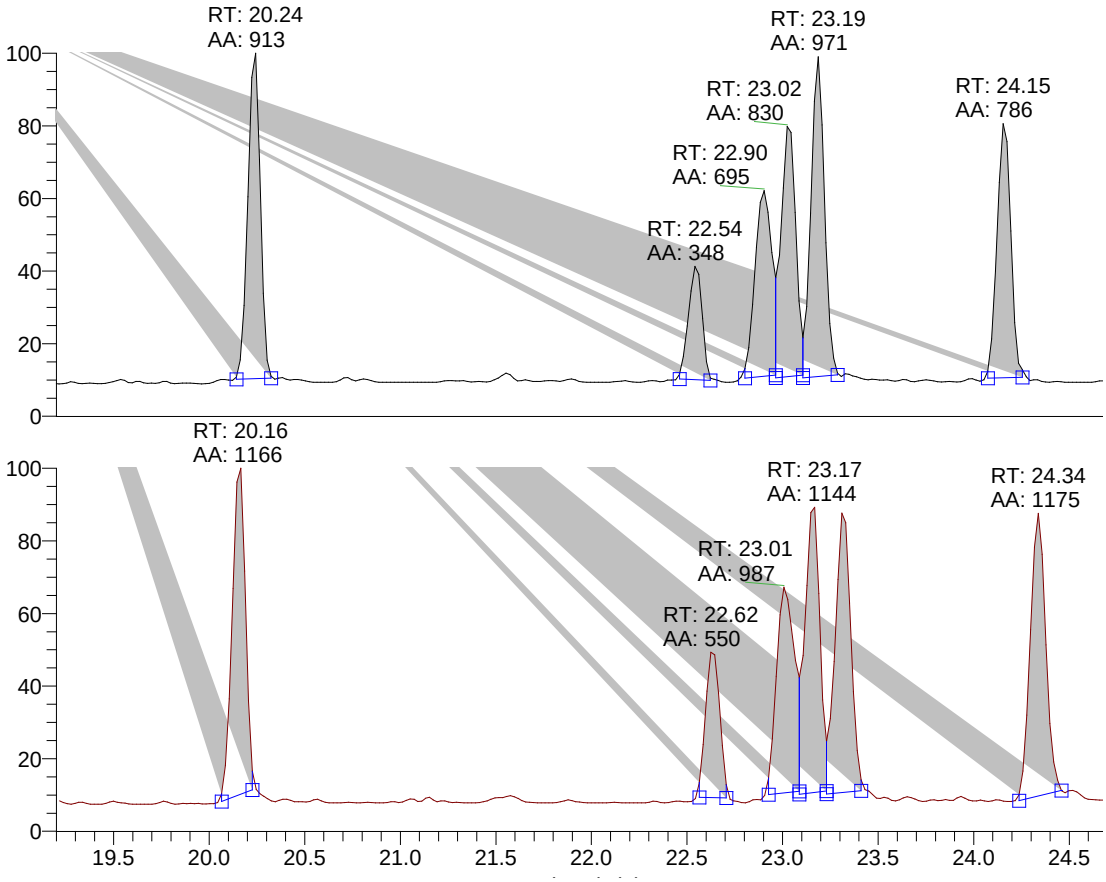

Figure 4. Peak shape of native TCDD using standard GC condition (upper chromatogram) and using DualData G2 MCD (lower chromatogram)

Problems of air accumulation in the helium supply line caused by micro leaks could be solved by continuously micro-purging the helium line by using a three way switching valve. Experiments showed that there was zero additional oxygen ingress to the MS system when using DualData G2.

The Thermo Scientific DualData G2 acquisition option can be used for different POPs analyses applications such as Dioxins, PCBs or PBDEs. Also a combination of different applications per GC is possible.

With an increase of more than 90% the sample throughput for Dioxins could almost be doubled.

Acknowledgements
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References

1. Method 1613 Rev.B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, (1994); *U.S. Environmental Protection Agency, Office of Water Engineering and Analysis Division,* Washington